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THE SYNTHESIS OF LOW TEMPERATURE PHASES BY THE CO-CONDENSATION OF THE ELEMENTS: A NEW SUPERCONDUCTING A15 COMPOUND, V_3Al.*

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A method is described whereby intermetallic phases which are not stable at high temperatures may be formed using controlled vacuum evaporation of the elements. V_3Al with the A15 structure was formed on substrates held at temperatures in the range 350-450°C. For the as-deposited sample the lattice parameter was 0.483 nm and the superconducting critical temperature was 9.6°K.

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In this note we describe a technique which overcomes several difficulties often encountered when conventional metallurgical methods are used to prepare certain combinations of the elements. The application of this technique to the search for new superconductors, in particular the phases with A15 (or Cr_3Si) structure, is discussed. Finally, we report the synthesis of A15 V_3Al, for the first time, and our measurements of its lattice parameter and superconducting critical temperature.[1]

Difficulties arise when conventional techniques, such as arc-melting or sintering, are used to combine elements with vastly different properties or when the reactions produce unwanted phases. For example, the maintenance of stoichiometry is a problem with high melting point compounds where one of the elements has a high volatility. In addition, some elements are troublesome in that container materials contaminate the sample. A more basic problem is the retention of a high temperature phase when it is cooled to a temperature below which it becomes metastable with respect to the desired phase. It now appears that some structures of scientific or technological interest are stable only at temperatures so low that the time required for formation is impossibly long.[2]

A method which has the potential to overcome these difficulties is the vacuum evaporation and co-condensation of the elements onto substrates maintained at a controlled temperature. In our work, the individual elements are evaporated from separate sources, usually by electron beam heating. Thus, vapor pressure differences are unimportant. With the localized surface heating provided by electron bombardment, either the element serves as its own crucible or contamination from the crucible is minimized. Contamination from the ambient atmosphere is minimized by

the high evaporation rates possible with electron bombardment. Deposition rates of one micron per minute are typical in the work reported here. The flux of each element is monitored by a chopped-beam ionization type rate monitor and controlled by a feedback loop to the electron beam source. With this technique, the ratio of the elements arriving at the substrate remains constant to within a few percent during the time required to deposit the sample. Thus, the correct composition at a particular place on the substrate is assured. Enhanced atomic mobility due to surface diffusion no doubt aids in establishing equilibrium and homogeneity at relatively low temperatures.

Examples of low temperature stability are found among the phases with the A15 structure. Of 35 systems for which data are readily available,[3,4,5] there are 17 for which the A15 phase is formed by a solid state reaction (i.e. at relatively low temperatures); the rest melt congruently or decompose pertectically. Thus, a number of A15 phases are formed peritectoidally and others, notably V_3Ga[6] and Nb_3Au,[7] are formed from the bcc solid solution as it is cooled. In addition, there are reports of new A15 phases (not included above) made at low temperatures with techniques such as solid state diffusion,[8] low temperature annealing of alloys,[9] and high pressure.[10,11] These techniques require a certain minimum temperature (usually 500-1000°C) in order to achieve reasonable reaction rates. There are still other systems for which electrochemical and size factors[2,12] do not prohibit formation of the A15 phases and yet it has not been observed, even when these low temperature methods are used. An explanation for this may be that the A15 phase in these systems is stable only below these minimum temperatures.

The V-Al system is one which should form an A15 phase. The bcc phase exists, in this system,[13] over an extended range of composition at high temperatures, which is also the case in the V-Ga system. From the considerations discussed above, we concluded that A15 V_3Al, if it existed, could only be formed at low temperatures. Until now, the A15 phase had not been positively identified in numerous experiments which utilized the usual methods mentioned above. This is despite the interest in V_3Al generated by Matthias, et al.,[14] with their announcement of $Nb_3(Al,Ge)$ and its high superconducting T_c, and their prediction that V_3Al "would be a very high superconductor." Holleck, et al.,[15] reported the formation of A15 V_3Al with a lattice parameter of 0.492 nm. However, attempts to repeat their result, using the same preparation methods, have failed to produce the A15 phase.[16,17] In addition, several points discussed by Holleck, et al., when examined in the light of work published subsequent to their article (in 1963), raise serious questions concerning their claim: (1) The Holleck,et al.,studies were concerned with the V_3Al-V_3Sb pseudobinary system. They pointed out the surprising fact that the measured x-ray intensities did not vary appreciably as Al replaced Sb on moving across the system; further, that the measured intensities for their reported V_3Al were in closer agreement with those calculated for V_3Sb rather than with those calculated for V_3Al. Because Sb has a much larger scattering factor than does Al, this is a very large effect. We calculated line intensities for a range of V_3Al-V_3Sb pseudobinary alloys, with corrections for anomalous scattering (Holleck,et al.,used Cr-Kα radiation), and found excellent agreement with observed intensities, for their reported V_3Al, at a composition near 40 mole % V_3Sb. (2) Their reported lattice

parameter, 0.492 nm, represents an unexpected 4% volume expansion over the solid solution, and is much larger than our measured value, 0.483 nm. Our value is in good agreement with predicted values and with values obtained by the extrapolation of data on pseudobinary alloys (see below). In addition, as noted by Holleck, et al., their lattice parameter did not vary appreciably as Al replaced Sb in the $V_3(Al,Sb)$ system. Indeed, their value of 0.492 nm reported for V_3Al is consistent with recently measured values for V_3Al-V_3Sb alloys.[18,19] Thus, both the x-ray intensities and the lattice parameter reported by Holleck, et al., for their V_3Al are consistent with those for a V_3Al-V_3Sb alloy and do not agree with our values for V_3Al. (3) Holleck, et al., report having made V_3Al at 1500°C followed by a 6 to 10 hour anneal at 1000°C. However, the work of Müller[18] on ternary alloys and our own results indicate that the V_3Al A15 phase is not stable above 700°C. However, the addition of Sb will increase the temperature at which the A15 phase can be formed.

For the purposes of this experiment, the substrate (glass, fused quartz, or alumina) was held at various temperatures in the range 350-450°C. The approximately 3 micron thick deposits required 3 minutes to make, after which the substrate heating power was immediately turned off to minimize possible contamination of the deposits. The background pressure in the all metal system during evaporation was 3×10^{-7} torr.

The use of an extended substrate allows one to make, in a single experiment, a considerable portion of the binary phase diagram. From the x-ray diffraction data of one run, we identified the following in decreasing order of their vanadium content: A2(bcc) solid solution, the A15 phase, A2 solid solution again, and the complex cubic phase V_5Al_8.

These different regions were usually apparent visually because of slight differences in reflectance and color. This visual identification during a slow heating experiment, in situ, indicated that the A15 phase is not stable above some temperature between 600 and 700°C, in agreement with the statements above. This most likely explains the failure of past attempts to synthesize V_3Al.

All of the strong diffraction lines expected for A15 V_3Al were observed in the region of the deposit with the composition V_3Al (as determined both by microprobe and thickness measurements). No extra lines, other than those attributed to the bcc solid solution, were observed. The lattice parameter of vanadium-rich A15 V_3Al was determined from a Debye-Scherrer powder pattern using material scraped from the two-phase region of the substrate. Nickel-filtered Cu-K radiation was used and the lattice parameter computed from observations above $2\theta = 60°$, using $\lambda(CuK\text{-}\alpha) = 0.154178$ nm and a least-squares extrapolation vs $1/\sin 2\theta$. The a_o was 0.4829 ± 0.0003 nm, near the values of 0.483 to 0.484 predicted on the basis of work on ternary alloys by Müller[18] and Asada, et al.,[19] and in agreement with our prediction of 0.483 nm based on the Geller radii.[12] A slight increase in the lattice parameter with increase in aluminum content indicates that the phase exists over a limited range of composition near 25 atomic percent Al. Table I lists the positions and intensities of the observed peaks (both taken from a microphotometer trace of the powder pattern) along with calculated intensities. The intensity ratios of adjacent lines agree remarkably well with the calculated values, except where lines from the vanadium solid solution interfere.

Thus far, the maximum critical temperature is 9.6°K, as measured resistively. The extent to which T_c can be increased by higher substrate temperature or annealing remains to be seen. We do not feel that it is meaningful to compare our T_c with values predicted on the basis of extrapolations in various $V_3M_xAl_{1-x}$ systems. These are characterized by a low predicted T_c if based on a V_3M with high T_c (e.g. Si, Ga),[18,19,20] and a high predicted T_c if based on systems for which V_3M has a low T_c (e.g., Ge, Sb, As).[18,21] However, we intend to determine the degree to which T_c can be increased by alloying.

In conclusion, we wish to point out the significance of the approach used successfully in this work: there are many other possible A15 compounds which may be stable only at relatively low temperatures. There is the real possibility that some of these may have high superconducting critical temperatures.

Addendum

Subsequent to the submission of this paper, we learned of the publication of Luo, et al.[21] Their extrapolated value of a_o for V_3Al, obtained from the study of ternary compounds $V_3(Al,X)$, agrees with our result. Our discussion concerning the stability of A15 phases in general, and V_3Al in particular, is similar to the ideas presented in their paper.

A new report has appeared[22] of the formation of A15 V_3Al, with a lattice constant of 0.4812 nm, and a T_c of 11.65°K. This material was annealed at 1000°C for 180 hours in a quartz ampoule. The authors found 1% Si in the sample as a whole. It is likely that the Si concentration was higher in the A15 phase, which was a small fraction of the sample. Only a few percent Si is required to make the reported lattice constant and T_c consistent with our results. As discussed previously, we do not believe that the pure V_3Al A15 phase is stable above $\sim$ 700°C, however it is possible that a few percent Si would permit formation of the A15 phase at 1000°C.

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REFERENCES

1. A preliminary account of this work was given in: HARTSOUGH, L. D., HAMMOND, R. H., LOOP, R., COLLVER, M., BREWER, L., PARKER, E. R., and ZACKAY, V. F., Bull. Am. Phys. Soc. 15, 1612 (1970).
2. BREWER, L., High Strength Materials, pp. 31, 39, 43, 51. John Wiley & Sons, New York (1965).
3. SHUNK, Francis A., Constitution of Binary Alloys, Second Supplement. McGraw-Hill, New York (1969).
4. ELLIOTT, Rodney P., Constitution of Binary Alloys, First Supplement. McGraw-Hill, New York (1965).
5. HANSEN, Max and ANDERKO, Kurt, Constitution of Binary Alloys, Second Edition. McGraw-Hill, New York (1958).
6. SHUNK, Francis A., Constitution of Binary Alloys, Second Supplement. p. 370. McGraw-Hill, New York (1969).
7. BUCHER, E., LAVES, F., MULLER, J. and VAN PHILIPSBORN, H., Phys. Lett. 8, 27 (1964).
8. SAVITSKII, E. M., BARON, V. V., and EFIMOV, Yu. V., Soviet Phys.-Doklady 11, 988 (1967).
9. VIELHABER, E. and LUO, H. L., Solid State Commun. 5, 221 (1967).
10. BANUS, M.D., REED, T. B., GATOS, H. D. LAVINE, M. C. and KAFALAS, J. A., J. Phys. Chem. Solids 23, 971 (1962).
11. KILPATRICK, D. H., J. Phys. Chem. Solids 25, 1213 (1964).
12. NEVITT, M. V., Electronic Structure and Alloy Chemistry of the Transition Elements, p. 125. Interscience (1963).
13. HANSEN, Mas and ANDERKO, Kurt, Constitution of Binary Alloys, Second Edition, p. 144. McGraw-Hill, New York (1958).

14. MATTHIAS, B. T., GEBALLE, T. H., LONGINOTTI, L. D., CORENZWIT, E., HULL, G. W., WILLENS, R. H., and MAITA, J. P., Science 156, 645 (1967).

15. HOLLECK, H., BENESOVSKY, F., and NOWOTNY, H., Monatsh. Chem. 94, 477 (1963).

16. KORNILOV, I. I. and MATVEEVA, N. M., Dokl. Akad. Nauk. SSSR 179, 870 (1968); Proc. Akad. Nauk. USSR 179, 298 (1968).

17. HARTSOUGH, L. D., unpublished results. (See also ref. 21).

18. MÜLLER, A., Z. Naturforsch. 24a, 1136 (1969).

19. ASADA, T., HORIUCHI, T. and UCHIDA, M., Japan J. Appl. Phys. 8, 958 (1969).

20. OTTO, G., Z. Physik 218, 52 (1969).

21. LUO, H. L., VIELHABER, E., and CORENZWIT, E., Z. Physik 230, 443 (1970).

22. SURIKOV, V. I., BORZITZKAYA, M. K., SCHTOLTZ, A. K., ZAGRAZSKII, V. L. and GELD, P. V., Fiz. Metall. Metallov. 30, 1167 (1970). We wish to thank Prof. H. L. Luo for bringing this to our attention.

Table 1. Observed and calculated intensities for V_3Al, with Cu-Kα radiation and anomalous scattering for vanadium.

hkℓ	2θ	I_{obs}	I_{calc}	Remarks
111	26.6	(20)	23	high background
200	37.5	64	48	
210	42.2	284	227	+(V)
211	46.3	100	100	
220	-	-	2	
310	-	-	3	
	61.2	24	-	(V)
222	67.4	56	25	
320	70.5	80	43	
321	73.6	100	45	
	76.9	128	-	(V)
400	79.7	48	23	
330,411	-	-	2	
420	92.6	56	14	+(V)
421	94.11	56	41	
332	96.94	18	11	
422	-	-	< 1	
431,510	-	-	3	
	106.71	48	-	(V)
432,520	118.58	88	55	
521	123.23	80	23	+(V)
440	129.07	40	32	
	143.16	96	-	(V)
530,433	-	-	1	
442,600	146.4	(16)	23	very weak, broad
610	151.75	32	36	
532,611	159.24	40	89	

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