The Synthesis of Low Temperature Phases by the Co-Condensation of the Elements: A New Superconducting A15 Compound, V-A1

Permalink
https://escholarship.org/uc/item/65k8016n

Authors
Hartsough, L.D.
Hammond, R.H.

Publication Date
1970-12-01
THE SYNTHESIS OF LOW TEMPERATURE PHASES BY THE CO-CONDENSATION OF THE ELEMENTS: A NEW SUPERCONDUCTING A15 COMPOUND, V₃Al

L. D. Hartsough and R. H. Hammond

December 1970

AEC Contract No. W-7405-eng-48

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
THE SYNTHESIS OF LOW TEMPERATURE PHASES BY THE CO-CONDENSATION OF THE ELEMENTS: A NEW SUPERCONDUCTING Al5 COMPOUND, V₃Al.

L. D. Hartsough and R. H. Hammond

Inorganic Materials Research Division, Lawrence Radiation Laboratory
University of California, Berkeley, California 94720

A method is described whereby intermetallic phases which are not stable at high temperatures may be formed using controlled vacuum evaporation of the elements. V₃Al with the Al5 structure was formed on substrates held at temperatures below 350°C. For the as-deposited sample the lattice parameter was 0.483 nm and the superconducting critical temperature was 8.5K.

*Research supported by the U. S. Atomic Energy Commission.
†Also, Department of Physics, University of California, Berkeley, Ca.
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 Al5 (or Cr3Si) structure, is discussed. Finally, we report the synthesis of Al5 V3Al, for the first time, and our measurements of its lattice parameter and superconducting critical temperature.

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.1

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. 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 Al5 structure. Of 35 systems for which data are readily available, there are 17 for which the Al5 phase is formed by a solid state reaction (i.e. at relatively low temperatures); the rest melt congruently or decompose peritectically. Thus, a number of Al5 phases are formed peritectoidally and others, notably V3Ga and Nb3Au, are formed from the bcc solid solution as it is cooled. In addition, there are reports of new Al5 phases (not included above) having been formed at low temperatures using techniques such as solid state diffusion, low temperature annealing of alloys, and high pressure. 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 do not prohibit formation of the Al5 phase and yet it has not been observed, even when these low temperature methods are used. An explanation for this may be that the Al5 phase in these systems is stable only below these minimum temperatures.
The motivation for searching for new Al5 phases is that some of these could have a very high superconducting critical temperature, based on available criteria for high $T_c$ among the known Al5 superconductors. The latter are the most numerous of the high $T_c$ materials and include $\text{Nb}_3(\text{Al,Ge})$ with a $T_c$ of 20.7°K, the present maximum. It is by no means certain that this value cannot be exceeded. Therefore, it is desirable to search for new Al5 compounds.

The V-Al system is one which should form an Al5 phase. Until now, the Al5 phase had not been positively identified in numerous experiments which utilized the usual methods mentioned above. This is despite the interest in $\text{V}_3\text{Al}$ generated by Matthias, et al., with their announcement of $\text{Nb}_3(\text{Al,Ge})$, and their prediction that $\text{V}_3\text{Al}$ would be a very high superconductor. Holleck, et al., claimed to have formed Al5 $\text{V}_3\text{Al}$ with a lattice parameter of 0.492 nm. Several attempts to repeat their results failed. It was concluded that Holleck, et al., had formed Al5 $\text{V}_3\text{Si}$ and/or other phases as a result of contamination from the hot pressing in carbon dies or subsequent annealing of their samples in fused quartz ampoules. To check the possibility that carbon, nitrogen or oxygen favors the formation of Al5 $\text{V}_3\text{Al}$, Müller added C, $\text{V}_2\text{O}_5$ and VN to $\text{V}_3\text{Al}$ samples. The products observed after heat treatment consisted of carbides and nitrides of vanadium, Al$_2$O$_3$, and the A2 (bcc) V-Al solid solution. The bcc phase exists, in the V-Al system, over an extended range of composition at high temperatures, which is also the case in the V-Ga system. From these considerations, we concluded that Al5 $\text{V}_3\text{Al}$, if it existed, could only be formed at low temperatures. This idea was recently supported by Müller's work on ternary alloys which suggested
to us that the Al5 phase would form at about 300°C.

For the purposes of this experiment the substrate (glass or fused quartz) was held at about 350°C. This is the temperature with the shutter closed; the substrate cools somewhat when the shutter is opened. The approximately three micron thick deposits were smooth and of mirror-like quality. The pressure 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 Al5 phase, A2 solid solution again, and the complex cubic phase V₅Al₈. These different regions were sometimes apparent visually because of slight differences in reflectance and color. All of the strong diffraction lines expected for Al₅ V₃Al were observed in the region of the deposit with the composition V₃Al (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 Al₅ V₃Al was determined from a powder pattern using material scraped from the substrate. The a₀ was 0.4830 ± 0.0003 nm, near the values of 0.483 to 0.484 predicted on the basis of work on ternary alloys by Müller and Asada, et al., and in agreement with our prediction of 0.483 nm based on the Geller radii. 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.

It should be noted that both of the substrates used in the work
contain the element silicon. It is possible that $V_3\text{Si}$, another Al5 phase, could have formed in a very thin layer at the surface of the substrate, and it cannot be ruled out that this could help in the nucleation of the $V_3\text{Al}$ Al5 phase. This will be studied in further work. However, in view of the low temperature, short time (180 sec), and the three micron thickness of the V-Al deposits, it is certain that the bulk of the film was $V_3\text{Al}$ with the Al5 structure, as determined by x-ray measurements. This is also indicated by the fact that the Al5 structure was found only at the $V_3\text{Al}$ composition, between bcc phases.

Thus far, the maximum critical temperature of 8.5°K, as measured resistively, is in approximate agreement with extrapolations from the studies of Otto,\textsuperscript{21} and Asada, et al.\textsuperscript{20} The extent to which $T_c$ can be increased by annealing remains to be seen. The critical temperature of Al5 phases is known to be strongly dependent upon the degree of order.\textsuperscript{22,23} For example, we prepared $V_3\text{Ga}$ in a similar fashion, with a substrate temperature of 350°C, and the $T_c$ was 12.3°K, as compared to the value of 14.5°K reported for well annealed samples. Similarly, $\text{Nb}_3\text{Sn}$ formed by co-deposition at 600°C had a $T_c$ of less than 14°K.\textsuperscript{24}

In addition to studying the effects of variations in the substrate, substrate temperature, and annealing, we will determine the degree to which $T_c$ can be increased by alloying.
ACKNOWLEDGMENTS

We wish to acknowledge the help and assistance of the staff at the IMRD, especially Mr. D. Whitaker. We are indebted to Dr. M. Pickus, Messrs. J. Roberts, M. Collver, and R. Loop for assistance and helpful discussions. This work was made possible by the encouragement and support of Professors L. Brewer, E. R. Parker, and V. F. Zackay.
REFERENCES


17. HARTSOUGH, L. D., unpublished results.
LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.