

FABRICATION OF ALUMINUM NITRIDE AND ITS STABILITY IN LIQUID ALKALI METALS*

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OBJECTIVE

The objectives of this task are to (a) evaluate several fabrication procedures for development of aluminum nitride (AlN) coatings on the candidate first-wall structural material V-5wt.%Cr-5wt.%Ti, (b) evaluate the stability of coatings in contact with the structural alloy and liquid Li at temperatures of 200-400°C, (c) measure the electrical resistivity of the coated films after exposure to liquid Li, (d) evaluate the effects of coating defects on electrical resistivity, and (e) establish in-situ repair procedures to maintain adequate electrical insulating properties of the coatings.

SUMMARY

AlN has been selected as a prime candidate to electrically insulate the V-alloy first wall in the self-cooled concept for ITER application. Detailed investigations were conducted on the fabrication, metallurgical microstructure, compatibility in liquid Li, and electrical characteristics of AlN material obtained from several sources. Coating fabrication methods included physical vapor deposition, reaction sputtering, ion-beam-assisted deposition, chemical vapor deposition, and a chemical route. Microstructural characterization of the coated samples was conducted by scanning electron microscopy, energy-dispersive X-ray analysis, and X-ray diffraction. Lithium compatibility studies were conducted in static systems by exposure of AlN-coated specimens to Li for several time periods. Electrical resistance measurements were made at room temperature on the specimens before and after exposure to liquid Li. The results obtained in this study indicate that AlN is a viable coating from the standpoint of chemical compatibility in Li, electrical insulation characteristics, and ease of fabrication, and that the coating should be examined further for fusion reactor application.

BACKGROUND

Extensive thermodynamic calculations have been performed to evaluate potential electrical-insulator candidates that are chemically compatible in liquid metals for use as a coating on first-wall and blanket structural material (1). The issues of compatibility of the liquid metal and the coating involves the (a) thermodynamic stability of the coating when contacted by the liquid metal; (b) extent of dissolution of the coating in the liquid metal, which is dictated by the solubilities of coating constituents (and structural material constituents, if uncoated material or bimetallic systems are used) in the liquid metal at temperatures and temperature gradients that are present in the system; and (c) degrees of interaction between the coating constituents and the reactants such as O, C, N, and H in the liquid metal, which can result in changes in chemistry of the coating, thereby altering the insulating characteristics. The requirement is that the product of insulator coating electrical resistivity times thickness should exceed a nominal value of $0.01 \Omega \text{ m}^2$ under operating conditions. This translates to a minimum resistivity value of $10^4 \Omega\text{-m}$ for a coating thickness of $1 \mu\text{m}$, or a resistivity of $10^3 \Omega\text{-m}$ for a coating thickness of $10 \mu\text{m}$. Based on resistivity values of the materials listed above, a coating layer $<1 \mu\text{m}$ thick of any of these materials would be adequate from the insulating standpoint, provided the resistivity is not reduced during operation, i.e., by irradiation. This report summarizes the ongoing work in the development of AlN coatings; additional details are presented elsewhere (2,3).

EXPERIMENTAL PROGRAM

Several possible approaches are being examined to develop an AlN coating on the structural material. Some of these are to (a) prealuminize the surface of the material by a (pack) diffusion process and subsequently convert it to nitride in an external gas atmosphere, (b) apply a physical vapor deposition

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process with and without bond coats, (c) use a chemical vapor deposition process at 600-900°C, (d) apply a low-temperature method that involves sequential reactions, (e) prealuminize the surface of the alloy and convert it to nitride in a high-N Li environment, (f) preexpose the material to liquid Al and convert it to nitride in Li, (g) form, in-situ, a coating in Li with high thermodynamic activity for Al and N, and (h) prealuminize a specimen of a structural material and nitride it by using a N₂ cover gas during exposure to Li.

Physical vapor deposition (PVD) was one of the methods used to develop AlN coatings on both bare and prealuminized specimens of V-5Cr-5Ti alloy. The coatings were produced by Midwest Research Technologies (MRT) of Wisconsin and by BIRL of Illinois. Coatings were also made by reaction sputtering in a N atmosphere at Argonne National Laboratory (ANL) and by ion-beam-assisted reactive evaporation at Cametoid Advanced Technologies, Inc. (CAT), of Ontario, Canada.

Coatings Deposited by MRT

Aluminum nitride was sputtered reactively, that is, an aluminum target was sputtered in a partial pressure of high-purity N₂, with Ar as the primary sputtering gas. Because the process takes place in a vacuum chamber and uses high-purity reactants, the product should be very pure. The process proceeds at a relatively low temperature and generally does not exceed ≈250°C. Initially, the chamber was pumped down to 2×10^{-6} torr before coating was started. Specimens of both bare and prealuminized V-5Cr-5Ti and the Al target were sputter cleaned for 6 min with high-purity Ar flowing at a rate of 45 cm³/min and a chamber pressure of 20 mtorr. Subsequently, the sputter deposition of AlN_x was done with a 1200-W RF power source for 10 h in an Ar-N₂ gas mixture at a chamber pressure of 23 mtorr. The sputtered specimens were cooled in vacuum overnight, and then the second side of the specimens was coated the same way.

Coatings Deposited by BIRL

Aluminum nitride coatings also were deposited with reaction sputtering by BIRL. Specimens of V-5Cr-5Ti alloy were used as substrate material, and were coated with AlN; some received an intermediate layer of TiN and an outer layer of AlN. An MRC 902M sputtering system was used, with control of the partial-pressure of the reactive gas (N₂) and arc suppression of the Al sputtering target. The target was powered by a DC supply, which was run at 5 kW. The Ar sputtering gas was maintained at a constant pressure of 8 mtorr during sputtering. The chamber was initially pumped down to 1×10^{-6} torr before coating began. The partial pressure of N₂ was controlled with an optical gas controller and maintained constant at 1.6×10^{-4} torr during coating. The substrate was biased to 150 V with an Advanced Energy power supply, the coating deposition rate was 1300 Å/min, and the maximum temperature during the coating operation was <200°C.

Coatings Made at ANL

Aluminum nitride coatings were also made at ANL, by reaction sputtering in a low-pressure N₂ atmosphere at 350, 400, and 450°C. The specimens were heated by passing an electrical current through the substrates. The thickness of the coating after 1 h of deposition was in the range of 0.8-1.4 μm; after 4 h of deposition, it was ≈5.2 μm. The coating covered the entire surface of the V-alloy specimen, and the layer was fairly hard. Coatings developed at 350 and 450°C tended to crack, but those developed at 400°C were fairly adherent, mechanically harder, and scratch resistant.

Coatings made by CAT

Deposition of single-layer and graded AlN coatings on a V substrate by ion-beam-assisted reactive evaporation was attempted at CAT. In this process, Al is evaporated and deposited either by resistive heating or by an electron beam source while the growing film is bombarded with accelerated N ions produced in an ion gun. A basic advantage of this technique is controllability of the flux (arrival rate) and energy of the ion species, independent of the rate of deposition of Al. In contrast, in plasma-based processes, the voltage, current, chamber pressure, and deposition rate are all interdependent. Ten AlN

coatings were deposited on a pure V substrate under a range of processing conditions.

Exposure to Lithium

Coupon specimens of V-5Cr-5Ti alloy, Type 316 stainless steel in bare and prealuminized condition, and AlN-deposited samples from several sources (discussed above) were exposed in a liquid-metal system. Weight change was measured to establish corrosion rates for the structural alloys and coatings as a function of temperature, time, and liquid metal chemistry. After exposure, the specimens were examined by a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray (EDX) analyzer and by X-ray diffraction. The coated specimens were examined to evaluate coating integrity after liquid-metal exposure, microstructural changes in coatings, coating/substrate interactions, and electrical insulation characteristics of the coatings.

RESULTS

Characteristics of Coated Specimens

MRT-deposited AlN layers were fairly compact and of uniform thickness in the range of 8-12 μm . The hexagonal AlN phase with an (002) orientation was dominant. No V nitride was detected because the substrate was at $<200^\circ\text{C}$ during the coating process. Even though the coatings were fairly adherent, early exposures of these coated specimens to Li resulted in complete disappearance of the coating layer by either spallation or dissolution. As a result, the coated specimens were given a thermal-hardening treatment at $700\text{-}900^\circ\text{C}$ prior to exposure to Li. As before, the hexagonal AlN phase with (002) orientation was dominant, but traces of the V_2N phase remained because of a reaction between AlN and V at the coating/substrate interface. X-ray diffraction data for AlN-coated V-alloy specimens, developed at ANL, also indicated that the coatings were hexagonal AlN with an (002) preferred orientation. The coated specimens, analyzed by CAT with the Rutherford backscattering technique, indicated that the N/Al ratio in the coatings ranged from 1.04 to 1.32.

Exposure to Lithium

Several AlN-coated V-alloy specimens from different sources were exposed to an Li environment at 300°C , after which detailed microstructural analysis of all specimens and X-ray diffraction analysis of selected specimens was performed. Further, electrical resistance of several of the Li-exposed AlN-coated specimens was measured.

Figure 1 shows a cross-sectional SEM photomicrograph and EDX depth profiles for Al, N, V, Cr, and Ti, of an MRT-supplied, AlN-coated V-5Cr-5Ti alloy specimen after a 430-h exposure at 300°C to an Li environment in which Ar- N_2 gas was bubbled for 24 h. It is evident that the coating was intact and appears dense and fairly adherent to the substrate alloy. The EDX analysis shows that the coating consists predominantly of Al and N, with almost no contamination from either the impurities in Li or the substrate constituents. Figure 2 shows a cross-sectional SEM photomicrograph, and EDX depth profiles for Al, N, V, Cr, and Ti, of an ANL-developed, AlN-coated, prealuminized V-5Cr-5Ti alloy specimen after 430 h of exposure at 300°C to an Li environment of normal purity. Figure 3 shows data for a similar specimen exposed to an Li environment in which was Ar- N_2 gas was bubbled for 24 h. The coatings are somewhat thinner in these specimens than in those obtained from MRT, but the integrity of the coating, adhesion to the substrate, and morphology of the coating are very good. Because these specimens were prealuminized, a thin layer of (Al, V) nitride seems to have formed as an intermediate layer during the coating process, primarily because the specimens were heated to $350\text{-}450^\circ\text{C}$ during coating in the ANL approach. A comparison of data from specimens exposed to Li with normal N content (Fig. 2) and to Li with N_2 bubbling (Fig. 3) shows that the morphology and composition of the two specimens are virtually identical. This indicates that N concentration in Li may not have a significant effect on coating performance, especially at 300°C . The AlN-coated specimens obtained from CAT, were also exposed to Li environments at 300°C . The coatings on these CAT specimens completely disappeared into the Li in 120 h of exposure, as evidenced by the high electrical conductivity of the specimens after exposure.



V, Cr, Ti alloy

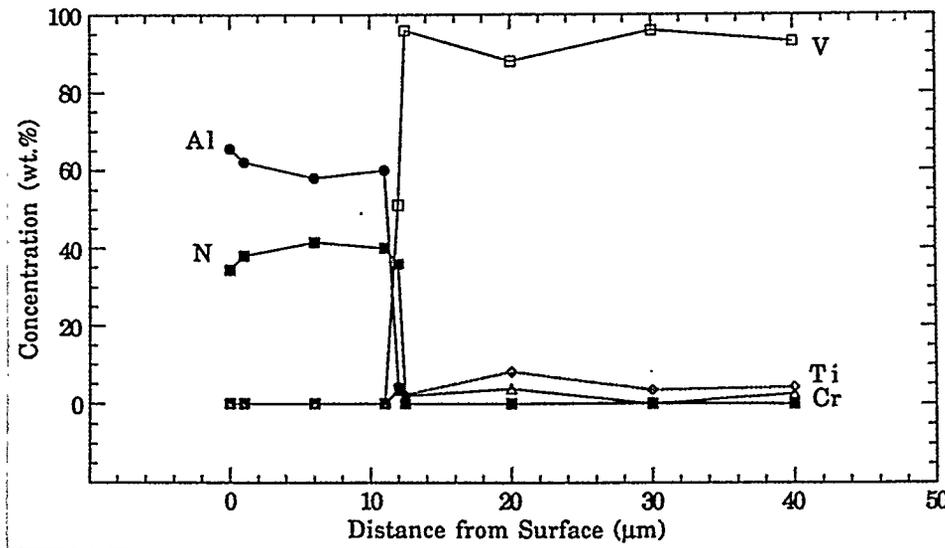


Figure 1. Cross-sectional SEM photomicrograph and EDX depth profiles for Al, N, V, Cr, and Ti for MRT-supplied, AlN-coated V-5Cr-5Ti alloy specimen after 430-h exposure at 300°C to Li environment in which Ar-N₂ gas was bubbled for 24 h

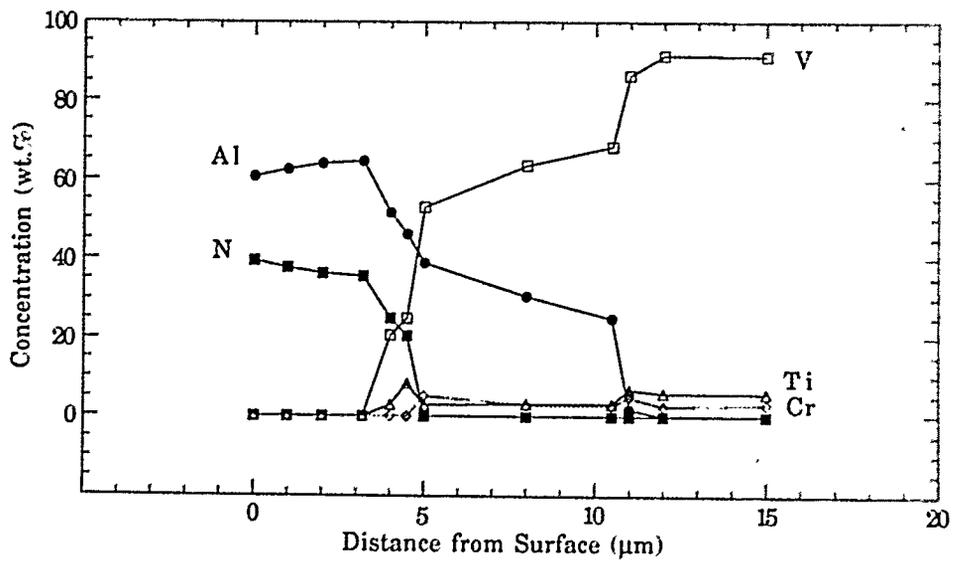
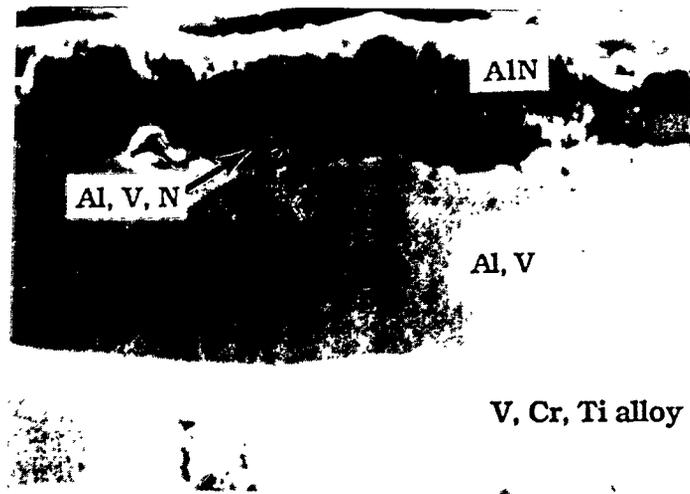


Figure 2. Cross-sectional SEM photomicrograph and EDX depth profiles for Al, N, V, Cr, and Ti for ANL-developed, AlN-coated, prealuminized V-5Cr-5Ti alloy specimen after 430-h exposure at 300°C to Li environment of normal purity

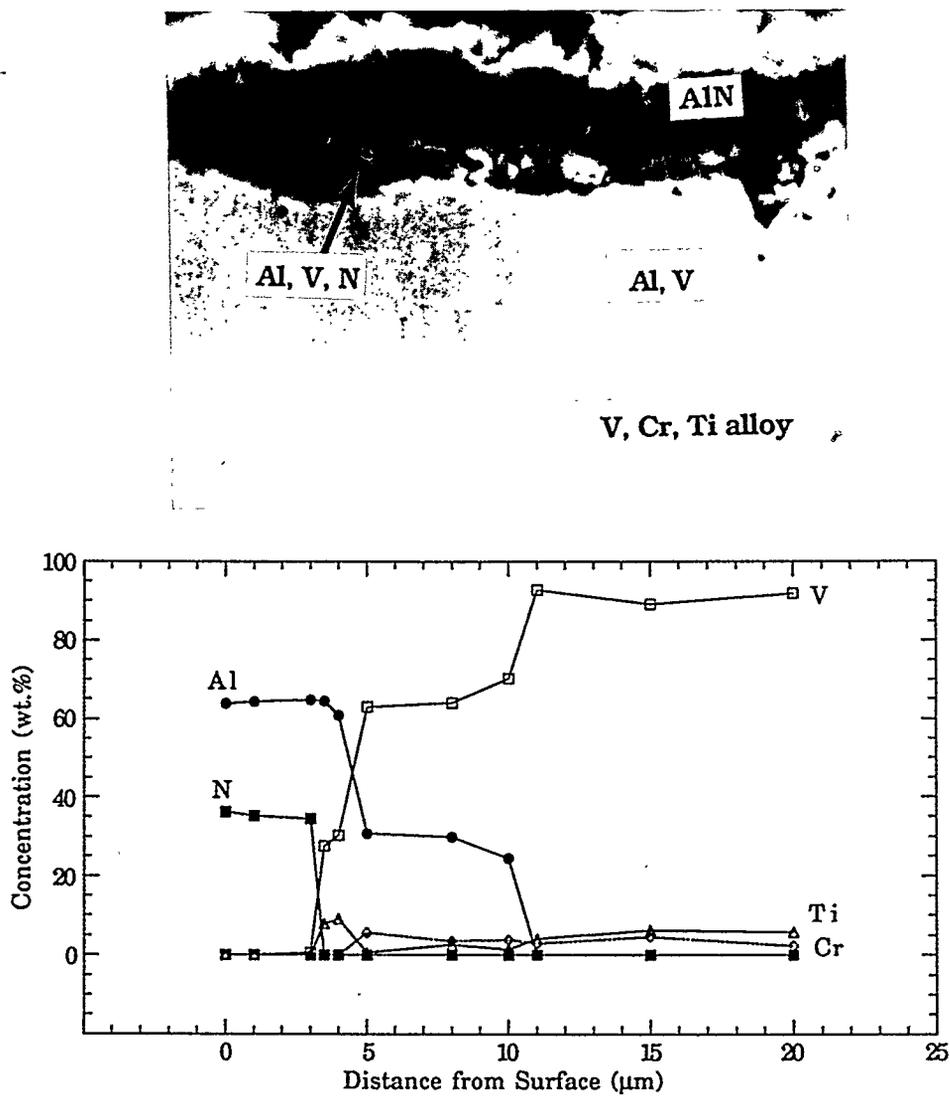
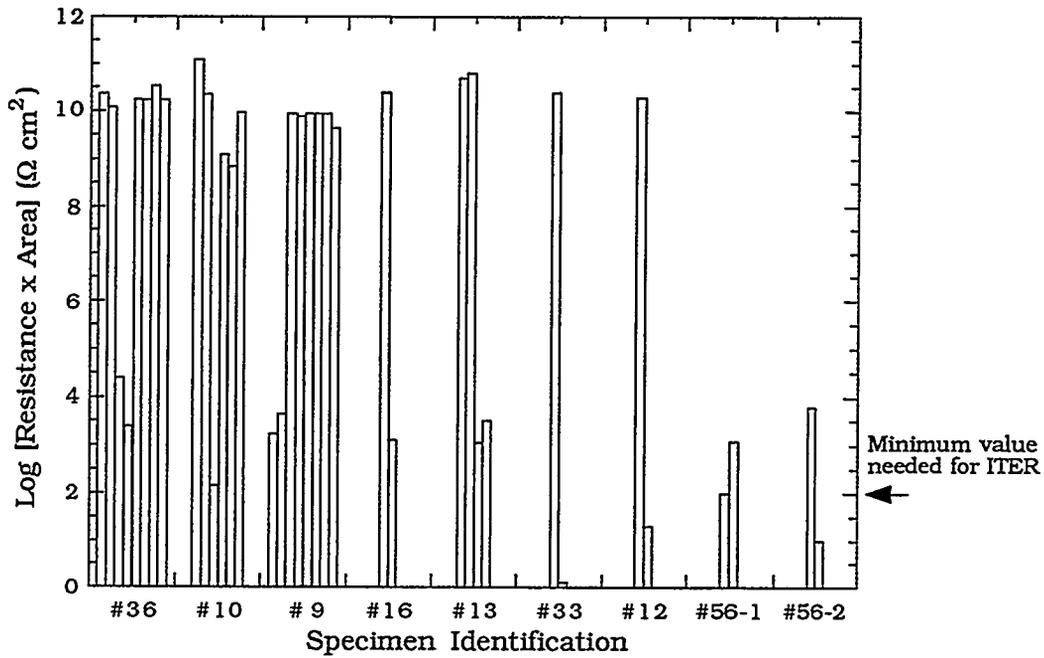


Figure 3. Cross-sectional SEM photomicrograph and EDX depth profiles for Al, N, V, Cr, and Ti for ANL-developed, AlN-coated, prealuminized V-5Cr-5Ti alloy specimen after 430-h exposure at 300°C to Li environment in which Ar-N₂ gas was bubbled for 24 h



Key to Specimen Treatment

- #36: V-5Cr-5Ti alloy, AlN coated
- #10: Alloy, AlN coated, hardened for 110 h at 900°C
- # 9: Alloy, AlN coated, hardened for 110 h at 900°C, exposed to Li for 600 h at 300°C
- #16: Alloy, prealuminized, AlN coated, hardened for 110 h at 900°C
- #13: Alloy, prealuminized, AlN coated, hardened for 110 h at 900°C, exposed to Li for 600 h at 300°C
- #33: Alloy, AlN coated, hardened for 284 h at 700°C, exposed to Li for 456 h at 300°C
- #12: Alloy, prealuminized, AlN coated, hardened for 284 h at 700°C, exposed to Li for 456 h at 300°C
- #56-1: Alloy, AlN coated by BIRL, hardened for 110 h at 900°C, exposed to Li for 600 h at 300°C
- #56-2: Alloy, AlN coated by BIRL, hardened for 284 h at 700°C, exposed to Li for 456 h at 300°C

Figure 4. Electrical resistance data for several AlN-coated specimens in as-coated and hardened conditions and before and after exposure to Li

Even though the corrosion performance of several AlN-coated specimens (especially MRT- and ANL-developed coatings) in an Li environment was good, some portions of the coatings seemed to crack and flake after exposure to Li. It was evident that the adhesion of the coatings developed by PVD/reactive sputtering processes is much lower than desired and that some improvement is needed to better bond the coating to the substrate and also to eliminate or minimize the porosity and microdefects in coatings developed by relatively low-temperature PVD processes. As a result, a thermal/chemical hardening treatment was attempted in which AlN-coated specimens were heated to 700-900°C in a controlled environment prior to exposure to the Li environments. Such an approach seemed to harden the coating, as evidenced by substantial improvement in scratch resistance of the coating surface. Several AlN-coated specimens were given a hardening treatment at 900 and 700°C and subsequently exposed to Li at 300°C. These coatings were also adherent and intact after exposure to Li.

After examination of the coating fabrication methods and the coating integrity in as-coated and hardened conditions and after exposure to Li environments, the next steps were to measure the electrical resistance of these Li-exposed, initially coated specimens and to compare the measured values with the minimum values required for ITER application. For this purpose, several specimens were selected for resistance measurements. Specimens included those that were initially bare and prealuminized condition, covered with coatings from various sources, subjected to various hardening treatments, and exposed to Li environments for several time periods. The specimens were masked and gold plated (as before) and resistances were measured at room temperature. Figure 4 shows the measured resistance values for several specimens and at different locations within the same specimen. Also shown in the figure is the minimum value for the resistance required for ITER application. The results show that the experimental approaches used in the present program can deliver coatings with adequate electrical resistance for application in Li-cooled fusion reactor blankets. Additional experiments and analysis of the coating procedures and coating/Li interactions are in progress to examine the long-term performance of these coatings in flowing Li environments and under irradiation conditions. At present, the coating is being applied by MRT to the internal surface of a 10-12 ft long pipe for proof-of-concept MHD testing to be conducted at ANL.

REFERENCES

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