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VOLATILITY FROM COPPER AND TUNGSTEN ALLOYS FOR FUSION REACTOR APPLICATIONS

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Abstract

Accident scenarios for fusion power plants present the potential for release and transport of activated constituents volatilized from first wall and structural materials [1]. The extent of possible mobilization and transport of these activated species, many of which are "oxidation driven", is being addressed by the Fusion Safety Program at the Idaho National Engineering Laboratory (INEL). This report presents experimental measurements of volatilization from a copper alloy in air and steam and from a tungsten alloy in air. The major elements released included zinc from the copper alloy and rhenium and tungsten from the tungsten alloy. Volatilization rates of several constituents of these alloys over temperatures ranging from 400 to 1200°C are presented. These values represent release rates recommended for use in accident assessment calculations.

Experimental ProceduresMaterial Preparation

Powder metallurgy processing was used to incorporate nonradioactive elements to represent those formed by transmutation processes. The compositions of the consolidated products are shown in Table 1. Powders for the copper alloy, which represented Cu-0.15Zr with compositional changes from one year of irradiation, were blended, mixed, sealed in a vacuum-tight container, and hot isostatically pressed at 138 MPa and 900°C for 2 h. The 6-mm thick compress was de-canned, hot-rolled in multiple directions to a final thickness of 2.0 mm, and prepared into 2.0 mm x 19.1 mm x 25.4 mm rectangular specimens. Powders of the tungsten alloy were blended, mixed, annealed in a 95% argon-5% hydrogen mixture at 300°C to reduce oxides, pressed into pellets, and hot sintered in hydrogen at 1500°C. The 10.4 mm diameter x 4.7 mm thick pellets, as well as the copper specimens, were ground to a 600 grit finish.

Testing and Analyses

The test procedure, described in more detail elsewhere [2], involved suspending a sample within a 38-mm diameter tube of high purity quartz that was positioned within the coil of an induction furnace. Either air at 2 standard liters per minute (SLM) or steam at 25 SLM was flowed upward past the inductively heated specimen. Temperature control was achieved with thermocouples and two-color infrared pyrometers. The copper alloy was tested at temperatures ranging from 400 to 1200°C at times of generally 1, 5, and 20 h. The tungsten alloy was tested at temperatures from 600 to 1200°C and durations ranging from 1 to 20 h. Testing was limited to a 20-h test at 600°C and a 1-h test at 1200°C due to oxidation rates. Volatilized species were collected on high purity quartz wool and on the walls at a cooler region of the vessel. Hydrofluoric acid was used to rinse the inner surfaces of the vessel and dissolve the quartz wool trap. Products in these solutions were then processed into water soluble species using a pyrosulfate fusion method and analyzed by atomic emission spectroscopy (AES) using an inductive coupled plasma (ICP).

The appearances and extent of oxide formation were checked following exposures in the respective environments. Surfaces of the copper specimens were

TABLE 1. ALLOY COMPOSITIONS, wt.%

Copper Alloy									
Cu	Ni	Zn	Co	Zr	Fe	Mg	Al	Mn	
91	4.5	2.1	1.0	0.9	0.14	0.16	0.11	0.11	
Tungsten Alloy									
W	Ni	Re	Fe	Co	Ta	Os	Cu	Mn	
95	2.3	1.1	1.0	0.55	0.15	0.06	0.05	0.05	

examined with a stereo microscope. Under certain conditions the oxide generated did not adhere, preventing weight change or oxide thickness evaluations. Adherent oxides on the tungsten alloy specimens, however, allowed oxide growth rates to be assessed by weight changes and thickness measurements from metallographic sections. Volatility rates in g/m²·h, were calculated from AES/ICP measurements, initial area of the specimen, and test duration.

ResultsCopper alloy

Specimens of the copper alloy exposed in steam remained relatively unoxidized at temperatures <1000°C. The surfaces exhibited some thermal etching and minor amounts of a reddish oxide, i.e., Cu₂O. Samples in steam that were heated to 1200°C in alumina crucibles melted and formed a porous whitish-grey oxide. Exposures in air resulted in the formation of black oxide, indicative of CuO, at all temperatures. The oxide, which increased progressively with time and temperature, was susceptible to spalling during cool down. A 0.6 mm thick oxide developed during the 5-h exposure at 1000°C. The 20-h exposure at 1000°C resulted in partial melting, but a general retention of shape. Melting would not be expected based upon the 1083°C melting point of copper and limited reduction in liquidus temperature to 1066°C due to oxygen. It may result from a high localized zinc concentration which would have a fairly strong influence upon the melting temperature. Samples tested at 1200°C in air melted into buttons which formed a fairly thick dark oxide.

Volatility measurements for many of the elements from the copper alloy exhibited considerable scatter. Except for zinc, these measurements lacked ordering with respect to exposure time and showed little temperature dependence. Maximum volatility rates for each constituent, without regard to exposure time or temperature, are therefore presented in Table 2 for each environment. These calculations, based upon the original surface area and 1-h exposures, represent worst cases and are proposed at the current time for use in accident assessment scenarios. Copper and nickel had the same volatilization rates in air as in steam. The rates for these elements were also somewhat proportional to their concentrations in the alloy. Some of the minor elements, cobalt, manganese, and iron, appeared to show higher volatility in steam, but magnesium and aluminum appeared to show the opposite trend. Zirconium was not found at levels

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TABLE 2. MAXIMUM OBSERVED VOLATILIZATION RATES FROM COPPER ALLOY BETWEEN 400 AND 1200°C, g/m²·ha,b

	Cu	Ni	Co	Zr	Fe	Mg	Al	Mn
Air:	5.3 E-1	4.4 E-2	9 E-3	<9 E-3	7.9 E-2	1.1 E-1	1.1 E-1	3 E-3
Steam:	5.3 E-1	4.4 E-2	1.8 E-2	<9 E-3	2.6 E-1	2.2 E-2	6.1 E-2	6 E-3

a. Assumed test duration is 1 hour.

b. Specimen area is $1.14 \times 10^{-3} \text{ m}^2$; weight, 8 g.

above the detectability limit. Zinc showed higher volatility rates in steam than in air as shown in Table 3. The rates in both environments progressively increased with temperature and included a marked increase upon melting at 1200°C as shown in Figure 1. The fraction of zinc released from this alloy at this highest temperature was approximately seven percent.

Tungsten alloy

The inductively heated tungsten alloy pellets exposed to flowing air formed a black, voluminous, adherent oxide (see Figure 2). Oxide scales formed perpendicular to surfaces due to isotropic growth at 600 and 800°C as shown by cross sections in Figures 2(a) and 2(b). Essentially direct access to the environment remained at the corners of the specimen. The growth of a similar oxide at 1000°C was even more pronounced, Figure 2(c). The sample tested at 1200°C formed a shiny, metallic product having platelike and dendritic formations, Figure 2(d), presumably resulting from the vapor phase of tungsten trioxide.

Oxidation kinetics were evaluated based upon weight changes and initial surface areas. Log-log plots representing change in mass per unit area (g/cm²) versus time (Figure 3) indicate a good fit of the 800 and 1000°C data to a cubic relationship. Alloy surface recession, which similarly indicated a cubic rate, was compared with a previously reported relationship [3]:

$$-dx/dt = (3.05 \times 10^2) \exp(-12,170/T) p^{1/2}, \text{ cm/h}$$

This equation was derived for the oxidation of tungsten for temperatures from 700 to 1300°C and pressures from 132 to 2.1×10^6 Pa. Good agreement exists between this relationship and the observed recession rate at 1200°C, see Table 4. The predicted values at 800 and 1000°C were within the range of observed values in the current study, but showed better agreement for the longer term, i.e., 5-, 10- and 20-h tests.

Volatile measurements from the tungsten alloy are summarized in Table 5. Many of the minor alloying elements, viz., tantalum, iron, manganese, and copper, did not show indications above detectability limits. Suggested volatility rates are presented based upon detection limits and a 1-h exposure. Nickel and cobalt exhibited limited volatility, except for the 1200°C test and the 1000°C/1-h test, which experienced a thermal cycle and possible temperature excursion. Subsequent investigations on a ferritic steel, HT-9, have demonstrated dramatic, order of magnitude increases in release of certain constituents as a result of cooling cycles which produce oxide cracking [4]. Rhenium and tungsten showed some volatility at all temperatures. The release of rhenium was systematic with respect to time and temperature. Tungsten release was limited at temperatures below 1000°C, but increased dramatically during the 1200°C test. Osmium, with its oxides of low melting points and high volatilities, was not detected in the test solutions and was presumed lost during pyrosulfate fusion processing.

TABLE 3. ZINC VOLATILIZATION RATES FROM COPPER ALLOY BETWEEN 400 AND 1200°C, g/m²·h

	400°C	600°C	800°C	1000°C	1200°C
Air:	7 E-3	1.8 E-2	2.3 E-2	3.1 E-2	9.6 E-0
Steam:	3.5 E-2	7.0 E-2	3.5 E-1	1.9 E0	11.4 E0

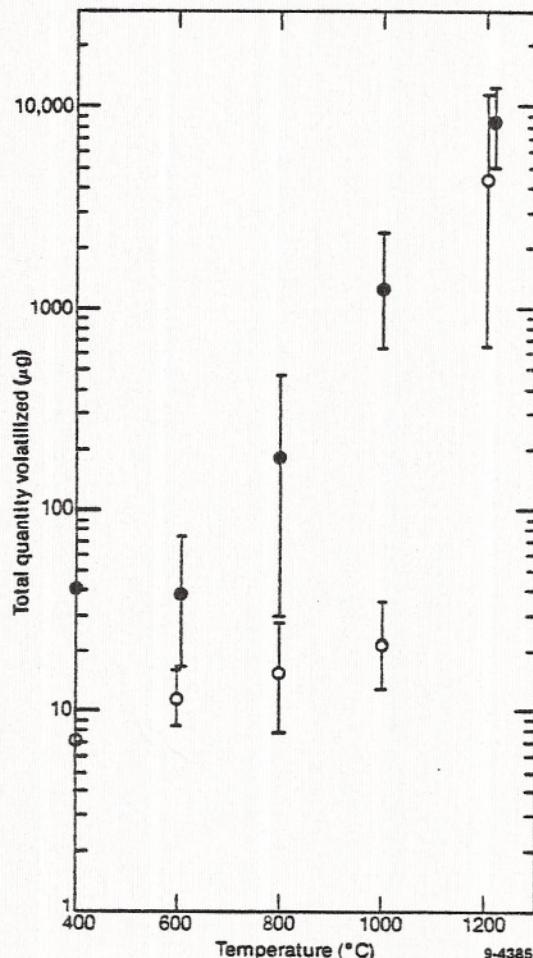


Figure 1. Zinc volatilization from copper alloy in air and steam environments at various temperatures.

Discussion

The volatilization studies on the copper alloy have shown that zinc is a primary actor. This element is not intentionally added as an alloying element; the 2 wt.% in the copper alloy studied is the amount which is expected to be generated by one year of irradiation. Furthermore, this element is very significant from the radiological safety standpoint [5]. Although present in small concentrations, this

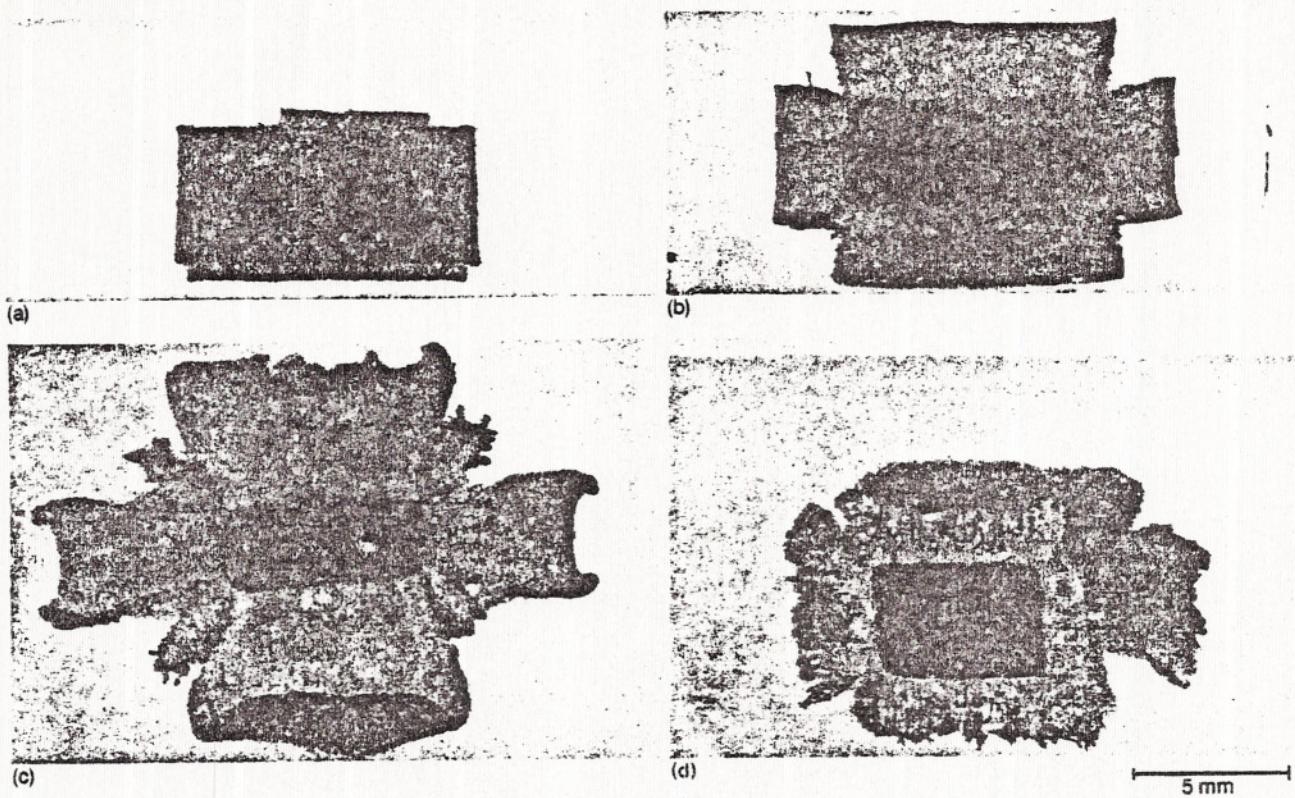


Figure 2. Cross sections of tungsten alloy specimens exposed to flowing air. a) 800°C for 1 h, b) 800°C for 20 h, c) 1000°C for 10 h and d) 1200°C for 1 h.

TABLE 4. COMPARISON OF TUNGSTEN ALLOY RECESSION RATES FROM OXIDATION, cm/h

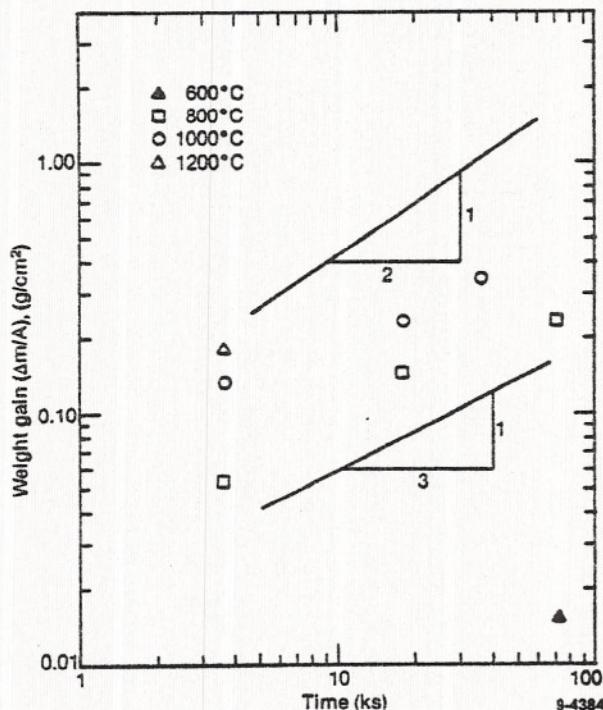


Figure 3. Weight gain data indicating a cubic rate for the W alloy at 800 and 1000°C.

element showed some of the highest releases, particularly at 800°C and above, and most notably upon alloy melting. The release was also higher in steam than in air at all but the highest temperature. The high vapor pressure of metallic zinc, i.e., approximately 20 Pa near its melting point of 420°C, and higher losses in steam than in air suggest that this element is being vaporized in this form. Also, the oxide scale, which developed in air, appears to retard the volatilization of zinc. Cobalt, iron, and manganese also showed some evidence of lower volatility in air. The volatility of aluminum and magnesium, on the other hand, appeared to be enhanced by the more oxidizing environment.

Reference [3]		
800°C	1000°C	1200°C
1.6 E-3	9.6 E-3	3.5 E-2

Current Study		
800°C	1000°C	1200°C
1.2 E-2 (1 h)	2.3 E-2 (1 h)	2.4 E-2 (1 h)
6.7 E-3 (5 h)	9.9 E-3 (5 h)	
3.0 E-3 (20 h)	9.3 E-3 (10 h)	

TABLE 5. VOLATILIZATION RATES DETERMINED FOR VARIOUS ELEMENTS FROM TUNGSTEN ALLOY, $\text{g}/\text{m}^2 \cdot \text{h}^2$

Element	600°C		800°C			1000°C			1200°C	
	20 h	1 h	5 h	20 h	1 h	5 h	10 h	1 h		
Ta	3.5 E-2 ^b									
Mn	1.1 E-2 ^b									
Cu	1.7 E-2 ^b									
Fe	2.5 E-2 ^b									
Ni	8.9 E-3 ^b									
Co	1.7 E-2 ^b									
Re	1.9 E-2	5.2	2.4	1.3	12.4	4.4	2.6	11.2		
W	1.4 E-2	1.2 E-1	6.8 E-4	1.4 E-2	1.2	5.4 E-2	5.1 E-1	36.4		

a. Specimen area is $3.5 \times 10^{-4} \text{ m}^2$; weight, 6 g.

b. Based upon detectability limit and one-hour exposure time.

The oxidation of the tungsten alloy showed some similarities and some differences from previous results. Expenditure rates of the tungsten showed good agreement with the work of Ong [3] (see Table 4). Other reports [6,7] of the oxidation process describe a paralinear behavior between 400 and 1100°C, and 700 and 1000°C, respectively. Mrowec and Werber [7] make reference to a two layered scale, an inner compact layer plus an outer porous portion. Rates are described as initially parabolic followed by a transition to a mixed or a linear rate. Reports indicate a transition to significant WO_3 evaporation above 1000°C [7] and 1100°C [6]. They indicate that this phase can reach an evaporation rate equivalent to its rate of formation. Oxidation rates in the current study did not show a transition from the cubic rate, even with consideration of decreasing surface area. An onset of significant volatilization, as evidenced by appearance and volatility measurements, did occur between 1000 and 1200°C in agreement with temperatures referenced above. The amount volatilized is much less than indicated in those reports, however. Based upon weight gain, the amount of WO_3 formed on the 1200°C test specimen is 880 $\text{mg}/\text{cm}^2 \cdot \text{h}$. The amount of WO_3 volatilized, as indicated by the rate shown in Table 5, is 4.5 $\text{mg}/\text{cm}^2 \cdot \text{h}$. This indicates a volatilization of $\sim 0.5\%$ of the WO_3 formed. The review by Schulze et al. [8] allow another comparison for volatilization rates. A rate of 0.14 $\text{mg}/\text{cm}^2 \cdot \text{h}$ was extracted from their data, which addressed temperatures from 1300 to 2500°C and low oxygen pressure, $2.8 \times 10^{-2} \text{ Pa}$. This rate, which is lower than that from the current study, might be expected due to the much lower oxygen pressure. Tungsten oxide volatility is undoubtedly complex and influenced by flow rate, oxygen partial pressures, and temperature gradients created in the oxide scale by internal heating and external cooling. Volatilities from the current experiment are likely lower due to cooler external surface oxide temperatures compared to values obtained under thermal equilibrium conditions. The current test conditions are, however, likely representations of radioactive decay heating resulting during potential accidents.

Volatilization measurements for the various elements from the tungsten alloy (Table 5) indicate that rhenium and tungsten are the primary elements released. Rhenium, although present at only one percent, showed rather substantial releases at and above 800°C. These releases increased fairly systematically with regard to time and temperature. It is expected that osmium would have shown a similar pattern of release. The volatilization of tungsten was somewhat uniform at temperatures through 1000°C and

then increased markedly at 1200°C. Fractional releases of rhenium and tungsten, for the maximum cases, are 14 and 0.2% of the contents within the specimen. This demonstrates the dependence of volatility upon specific constituents and some correlation to the low melting points and high volatilities of their derived oxides.

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