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SODIUM DEPLETION ON GLASS SURFACES DURING AUGER ANALYSIS

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ABSTRACT

The kinetics of the depletion of sodium on glass surfaces during Auger Electron Spectroscopic analysis is investigated. The decay process is mathematically represented as a sum of two single decaying exponential functions. This behavior may be described by a mechanism that accounts for the neutralization of sodium ions by the electron beam. Sodium ions and neutral sodium atoms are depleted by several known processes.

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1. Introduction

The analysis of glass surfaces is extremely important in the determination of various corrosion processes acting upon glass-immobilized nuclear waste in underground repositories. In particular, the analysis of various alkali and alkaline earth ions, especially sodium ions, is of great importance to the determination of the mechanism of glass leaching by groundwater. One widely used method of glass surface analysis is Auger Electron Spectroscopy (AES), coupled with argon ion sputter etching [1-4]. This technique is capable of determining glass composition at various depths from the glass surface.

Early work using AES on glass demonstrated an inability to detect sodium, although large concentrations were known to be present [5,6]. This was explained by the fact that the electron beam of the Auger analyzer caused a negative charge build-up below the glass surface in the manner first proposed by Lineweaver [7]. The sodium ions migrate away from the surface toward the region of negative charge. Other effects, such as stimulated electron desorption and localized heating, also give rise to the loss of sodium from the glass surface during AES analysis.

Electron microprobe studies indicate that the kinetics of the sodium removal process follow an exponential decay, preceded by an incubation period, during which the concentration of sodium ions remains constant [8-10]. In one AES analysis, however, the portion of the curve following the incubation period was represented by the form A [1-B ln (t/t_0)] in which t_0 is the incubation time, t is $>t_0$, and A and B are constants [2].

In this study, AES was used to probe the sodium removal process in two types of glass. The experimental evidence suggests that this process is characterized by a sum of two exponential decay curves, each with different decay constants and pre-exponential factors. These results are interpreted within the context of the mechanism proposed by Lineweaver [7].

2. Experimental Measurements

Measurements were carried out on two types of glass, with compositions shown in table 1. The glass buttons, 5/8 inch in diameter by 1/8 inch thick, were polished to 600 grit, mounted on a thirty-degree carousel, and placed in the bell jar of a Physical Electronics Model 545 Scanning Auger Microprobe, which is equipped with a cylindrical mirror analyzer. All of the data were obtained at room temperature.

The surfaces of the glass buttons, once placed into the spectrometer, received no further treatment. In particular, argon ion bombardment of the glass surface was avoided, since this technique can alter the physical and chemical properties of the glass surface. With argon ion bombardment, there is a possibility that sodium ions may be reduced to sodium metal, complicating the experimental results obtained with the analyzer beam. A suitable position for analysis was determined with elastically scattered electrons. The beam energy and current were adjusted prior to the electron beam shut-down. Once the analyzer beam was turned off, the sample was moved to a new position so that another portion of the sample was analyzed. The moment that the electron beam was reactivated was considered as zero time for kinetic analysis.

3. Results and Discussion

Figs. 1 and 2 show plots of the $\log_e$ of the sodium peak height (in arbitrary units) versus the analyzer beam bombardment time. Fig. 1 shows the sodium decay characteristics of the surface of Glass A; fig. 2 represents the removal of sodium from Glass B. The important feature to note is that for each of these curves, there are two distinct linear segments. For the data shown in figs. 1 and 2, the incubation period preceding sodium removal from the glass surface was negligible. During the course of these studies, however, experimental conditions were found in which the incubation period was observable.

The presence of the two linear portions in the decay curve is indicative of a mathematical expression of the form

$$A_i = A_1 \exp(-\alpha\, t_i) + A_2 \exp(-\beta\, t_i) \qquad (1)$$

The exponents α and β along with coefficients A_1 and A_2 can be determined. The linear segment at longer bombardment times is extrapolated to zero time. For this line segment, the first exponential term is negligible and the contribution is due only to the second term. A least-squares determination of the slope of the extrapolated curve gives a value for β, and the intercept corresponds to A_2. A_1 and α are determined by subtracting the expression $A_2 \exp(-\beta t_i)$ from the data points A_i in the short time portion of the curve and performing a least squares analysis on the resulting line. Table 2 lists the calculated values of α, β, A_1, and A_2 for the curves in figs. 1 and 2.

The data for Glass A (see table 2) show that as the beam current and voltage are increased, the magnitude of intercept A_1 decreases and that of A_2 increases. In Glass B, in which only the beam voltage is increased, A_2 and A_2 behave as Glass A. The temperature rise of the glass surface at the center of the beam was approximated from the formulas of ref. 11 to be 26 degrees for a 4-keV, 5-μA beam of 1-mm^2 area. These data indicate that the double exponential decay is independent of the glass composition (within the limits of this small sampling). Also, a second species is formed directly or indirectly from the first (presumably sodium ions on the surface), while electrons from the analyzer beam may take part in this interconversion. Temperature effects appear to be minimal.

The double exponential decay of eq. (1) can result from the conversion of sodium ions initially present on the glass surface to another species, with subsequent removal of both species. This is an example of a consecutive reaction mechanism. Lineweaver [7] has pointed out that two types of sodium species are present during the interaction of the glass and the electron beam. These species are sodium ions and neutral sodium atoms, formed by the reduction of sodium ions by the electron beam. The presence of neutral sodium atoms produces the brown discoloration of glasses when they are bombarded with electrons. Although Lineweaver's mechanism operated at beam voltages between 10 and 27 keV, Dawson has shown that the same mechanism can occur at beam voltages as low as 0.1 keV [12]. Electron browning is found to occur below the glass surface, but it is not inconceivable that electrons impinging on a glass surface reduce a number of the sodium ions found on the surface. The reduction of surface sodium ions by the electron beam may account for the consecutive reaction mechanism indicated by the double exponential decay described above.

No direct evidence for the presence of neutral sodium atoms was obtained. Neutral sodium atoms possess an $L_{2,3}VV$ Auger transition at 27 keV [13], but this transition was not observed. The complexity of the glass Auger spectrum in this region may have masked the presence of this peak.

In terms of a mechanism for the compositional change of sodium during AES analysis of glass, the following scheme is proposed

$$Na^+ (S_1) + e^- \xrightarrow{k_1} Na^o (S_1) \qquad (a)$$

$$Na^o (S_1) + e^- \xrightarrow{k_2} Na^+ (S_1) + 2e^- \qquad (b)$$

$$Na^+ (S_1) \xrightarrow{k_3} Na^+ (S_2) \qquad (c)$$

$$Na^o (S_1) \xrightarrow{k_4} Na^o (S_2) \qquad (d)$$

S_1 represents the glass surface affected by the electron beam, and S_2 represents any area not affected by the beam. In reactions a and b, the beam current density and beam voltage remain constant over time, and these reactions can be represented by a pseudo-first-order equation. Rate constants k_1 and k_2 will depend on the beam current density and beam voltage. Constants k_3 and k_4 represent the total removal rate constants of both Na^+ and Na^o, respectively. Since Na^o is not affected by an accumulation of negative charge beneath the surface, processes such as stimulated-electron desorption and thermal desorption are probably the dominant removal mechanisms.

The rate equations describing the removal of Na^+ and Na^o are

$$\frac{d[Na^+]}{dt} = k_2 [Na^o] - (k_1 + k_3) [Na^+] \qquad (2)$$

$$\frac{d[Na^o]}{dt} = k_1 [Na^+] - (k_2 + k_4) [Na^o] \qquad (3)$$

Solution of these equations, with $k_5 = (k_2 + k_4)$, $k_6 = (k_1 + k_3)$, and boundary conditions given by $[Na^+]$ (0) = $[Na^+]_o$ and $[Na^o]$ (0) = 0, produces the following expressions

$$[Na^+]\ (t) = \frac{[Na^+]_o\ k_5}{r_1 + r_2} \quad (r_1-1)e^{-r_1 t} + (1-r_2)e^{-r_2 t} \qquad (4)$$

$$[Na^o]\ (t) = \frac{[Na^+]_o\ k_1}{r_1 + r_2} \quad e^{-r_2 t} - e^{-r_1 t} \qquad (5)$$

$$r_{1,2} = \left| [-(k_5 + k_6)+, - \left((k_5 + k_6)^2 - 4\ (k_1\ k_2 - k_5\ k_6)\right)^{1/2}]/2 \right| \qquad (6)$$

This mechanism predicts the mathematical form that was determined experimentally. The exponent r_2 represents the value of β in eq. (1), and r_1 represents α. Coefficients for the exponentials containing r_2 and r_1 correspond with A_2 and A_1, respectively. According to table 2, the value of A_1 decreases with increasing beam current density and beam voltage, while A_2 simultaneously increases. Coefficient A_1, therefore, is assigned to the exponential term describing sodium ion decay; A_2 represents the coefficient for sodium metal decay.

4. Conclusion

The interaction of an electron beam from an AES analyzer with a glass surface causes sodium to deplete in a manner that can be described by the sum of two exponential decay components. the proposed mechanism that gives rise to this behavior is the neutralization of surface sodium ions by the electron beam.

Neutralization is followed by removal of sodium ions and neutral atoms by migration, simulated electron desorption, and localized heating. Kinetic analysis of this mechanism shows that the predicted mathematical form matches the form found experimentally.

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TABLE 1. Compositions of Glasses Used in This Study

Glass	Compound	Weight Percent
A	SiO_2	52.5
	B_2O_3	10.0
	Na_2O	18.5
	Li_2O	4.0
	CaO	5.0
	TiO_2	10.0
B	SiO_2	37.3
	B_2O_3	7.2
	Na_2O	15.0
	Li_2O	3.0
	CaO	4.7
	TiO_2	7.2
	Fe_2O_3	13.4
	Al_2O_3	2.8
	MnO_2	3.8
	NiO	1.8
	Na_2SO_4	0.4
	AW500*	2.4

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* A mixture of $CaAl_2Si_4O_{12} \cdot 6\ H_2O$ and (Ca, Na_2, K_2) $Al_2\ Si_{10}\ O_{24} \cdot 7H_2O$

TABLE 2. Analyzed Data from Figures 1 and 2*

Glass	Beam Voltage (keV)	Beam Current (μA)	α (min^{-1})	β (min^{-1})	A_1 (arbitrary)	A_2 (arbitrary)
A	3.0	0.16	0.09 (0.03)**	0.33 (0.07)	2.53 (.05)	0.59 (.08)
	4.0	3.78	0.32 (0.03)	1.30 (0.07)	1.85 (.04)	1.33 (.07)
B	3.0	5.00	0.65 (0.04)	1.27 (0.06)	2.10 (.04)	0.68 (.07)
	4.0	5.00	0.70 (0.05)	1.50 (0.09)	1.80 (.03)	1.06 (.08)

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* Coefficients A_1 and A_2 and exponents α and β correspond to Equation (1) in the text.

** Numbers in parentheses indicate relative errors.

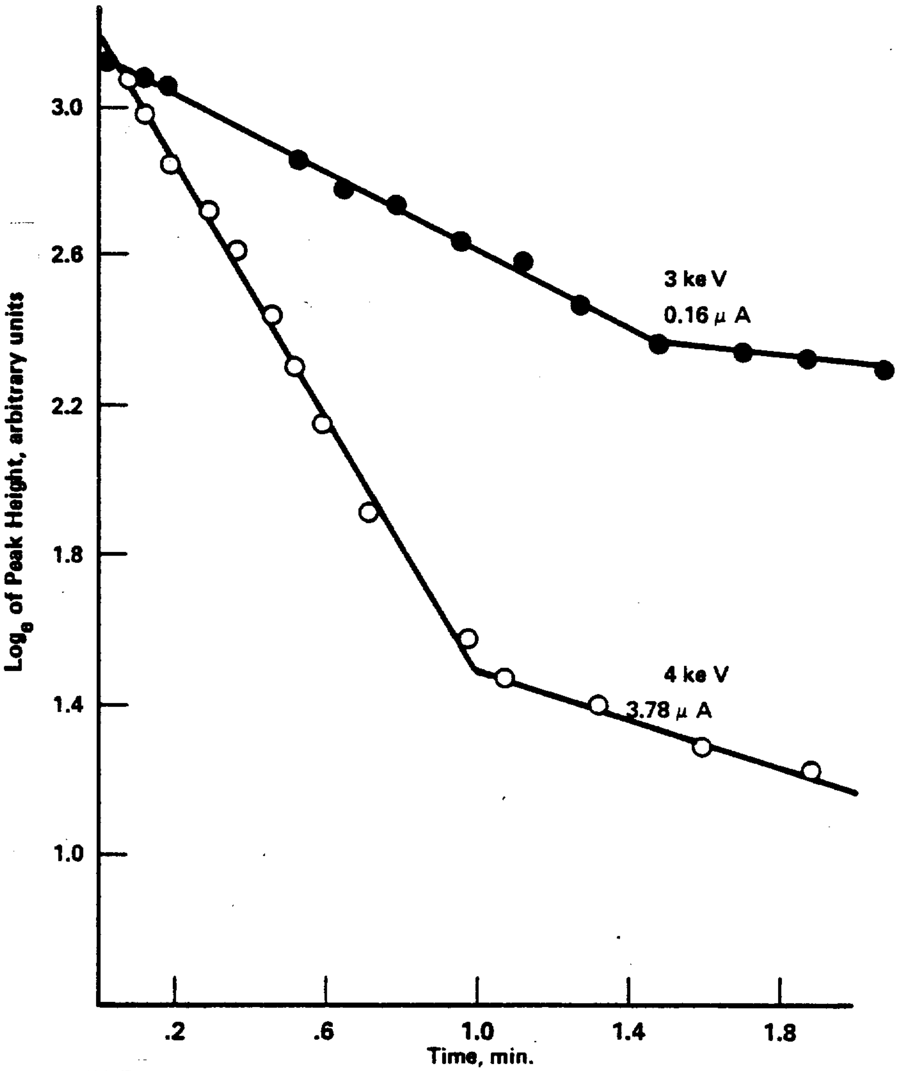

Fig. 1. Plot of Log$_e$ of Peak Height Versus Time for Glass A

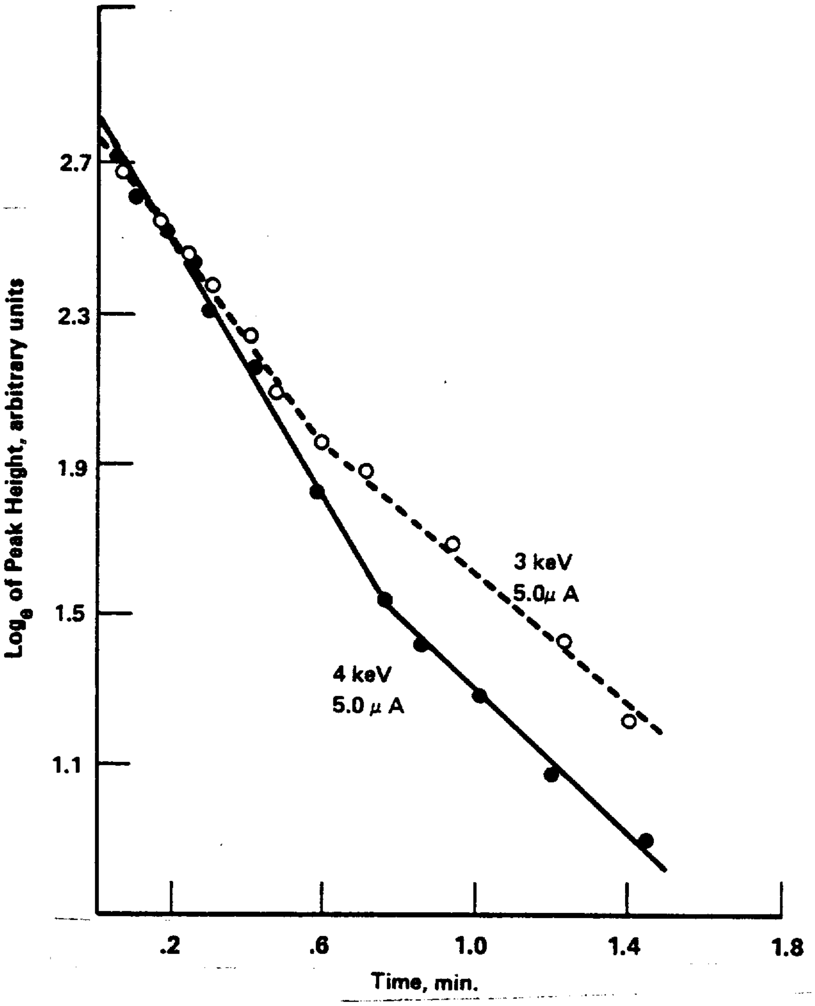

Fig. 2. Plot of Log$_e$ of Peak Height Versus Time for Glass B

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