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Behaviour of interstitial impurities on the surface of yttrium during solid state electrotransport: Auger studies

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Abstract

Investigations of electromigration of interstitial impurities O, C and N on the yttrium surface during solid state electrotransport in ultrahigh vacuum have been carried out by the method of Auger electron spectroscopy. It was shown that the behaviour of impurities on a surface correlated with that in the bulk during the electrotransport and a considerable segregation of O and C was taking place on the surface at reduced temperature. The analysis of possible mechanisms of the segregation has revealed non-equilibrium segregation as the most probable reason for the segregation. The parameters determining the segregation have been estimated.

Keywords: Interstitial impurities; Yttrium; Solid state electrotransport; Auger studies

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1. Introduction

At present the purest samples of rare earth metals, yttrium in particular, are obtained by the method of solid state electrotransport (SSE) [1,2]. Further increases in efficiency of purification by the SSE method are closely associated with the phenomena occurring on the metal surface. During the SSE process in vacuum the surface of a sample is in direct contact with the components of residual gases (O, N, CO, CO_2 etc.). The adsorption and desorption of gaseous impurities, their diffusion in the bulk of a sample and to the sample surface as well as chemical reactions taking place on the surface play a significant role. The study and comprehension of the behaviour of impurities on the surface provide additional possibilities for making metals purer.

2. Experimental

The SSE was carried out in the analytical chamber of an Escalab-5 electron spectrometer (hemispherical analyser) with a specially designed sample holder which enabled in situ investigations of the surface of yttrium (during SSE) by Auger electron spectroscopy (AES). Yttrium reduced from its anhydrous chloride by lithium in the vapour phase was used for the investigation. The impurity composition of the metal after electron beam melting is presented in Ref. [3]. Oxygen, carbon and nitrogen at 0.34 at.%, 0.029 at.% and 0.024 at.% in content respectively are the dominating impurities. Industrial purity yttrium was also used for the study; this contained a higher content of impurities, for example the content of oxygen was 2.8 at.%. The samples were made as $38\times2\times0.8$ mm^3 V-shaped strips and fastened to current leads by Ta adapters of 1.5×0.5 mm^2 cross-section. The tantalum was preliminarily annealed in high vacuum for 24 h at 2300 K.

The temperature of the sample and adapters was about 1350 K during SSE and the current density was about 700 A cm^{-2}. The composition of residual gases was checked by the quadrupole QX-200 mass spectrometer. The residual pressure in the analytical chamber was about 2×10^{-7} Pa. Auger electron spectra were obtained at primary beam energies of 3 and 5 keV, modulation energy 4 eV, primary beam current 1 μA, and beam diameter 100–200 μm. The concentration of elements on the surfaces of anode (Y^+) and cathode (Y^-) regions of the yttrium sample and on the tantalum adapters (at the points where they were attached to a sample) was determined by the method described in

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Ref. [4]. The lines at $E_C = 272$ eV, $E_O = 510$ eV, $E_N = 383$ eV, $E_{Cl} = 184$ eV, $E_S = 152$ eV, $E_Y = 127$ eV and $E_{Ta} = 179$ eV were used as analytical lines, the sensitivity being 0.5–1 at.%. The ion bombardment of samples was applied with an ion energy of 10 keV and of current 50–150 μA to estimate the depth distribution of impurities.

3. Results and discussion

The SSE experiments permitted observation (as far as the sensitivity of the AES method provides) of only the change in C, O, N, S and Cl impurity distributions, because the bulk concentrations of these impurities are one or two orders of magnitude higher than those of metallic impurities. The qualitative data on the segregation of impurities on the surface of a sample which is cooled are similar for both industrial purity and specially prepared Y samples of higher purity. However, because of the sensitivity of the AES method the redistribution of the above-mentioned impurities could be observed only on the industrial purity samples during SSE. Therefore, presented in Table 1 are the data for industrial purity yttrium. During the initial stage of electrotransport outgassing under ultrahigh vacuum conditions plays a significant role in redistribution of impurities. The surface concentrations of O, N, C and Cl decrease several times at the anodic and cathodic parts of a sample and hydrocarbons and oxide impurities, which are always present during the preparation of samples for the experiment, are removed. This is confirmed by the results of pressure changes in the chamber and the analysis of residual gases. The growth of peaks with the mass numbers 2, 12, 14, 16, 28 and 44 in the spectra of residual gases indicates the release of hydrogen, hydrocarbons, nitrogen, carbon oxide and dioxide. Hydrogen was removed most intensively during the initial stage for several hours. Analogous processes take place on the adapters as well, in addition to which a considerable amount of sulphur was discovered on both of the tantalum adapters. After 20–25 h the outgassing process is completed and only O and C impurities can be detected on the surface, their contents at the anodic part of the sample being slightly higher than that at the cathode. A noticeable accumulation of these impurities (compared with the anodic part) occurs at the anodic part during SSE. The concentration of oxygen and carbon increased 3–4 times after 44 h at the anodic part whereas this did not occur at the cathodic region, the bulk O and C diffusion occurring in the anodic direction [5] during SSE. This fact may be explained by both the correlation of bulk and surface content of these impurities and their probable diffusion to the anode.

Table 1
Distribution of impurities on the surface of yttrium and tantalum adapters during solid state electrotransport

Impurity		Concentrations (at.%) of impurities at the following times and vacuum pressures [a]				
		0.1 h, 1.1×10^{-5} Pa	16 h, 6.6×10^{-7} Pa	24 h, 4.0×10^{-7} Pa	46 h, 2.6×10^{-7} Pa	68 h, 2.0×10^{-7} Pa
Ta_+	O	11	12(10)	8(10)	9(11)	8(5)
	C	51	34(32)	28(33)	26(27)	24(31)
	S	31	17(17)	18(19)	20(18)	19(20)
	Y	2	3(3)	3(4)	4(7)	3(5)
Y_+	O	33	8(32)	2(27)	7(27)	8(27)
	C	16	7(45)	3(45)	4(41)	8(42)
	N	14	4(5)	1(5)	– (6)	– (6)
Y_-	O	23	1(24)	– (16)	– (24)	– (17)
	C	32	5(53)	– (54)	– (40)	1(54)
	N	9	– (3)	– (5)	– (5)	– (4)
Ta_+	O	8	13(11)	14(15)	10(13)	12(15)
	C	59	34(37)	34(27)	34(34)	34(36)
	S	11	14(17)	6(19)	10(14)	10(10)
	Y	–	4(4)	3(8)	6(8)	5(6)

[a] Values in parentheses represent the concentrations of elements during the cooling of specimens.

Determination accuracy, ±10%.

Any noticeable redistribution of impurities was not revealed on tantalum adapters during the experiment, probably because of the low temperature for this metal. It is known that the impurities O, C and N segregate on the surface of metals at certain temperature conditions [6]. To investigate the segregation of impurities on the Y surface the current was either switched off or reduced during the electrotransport until the required temperature was attained and a concentration of impurities was determined on a surface. It was found that after 1–2 min a noticeable segregation of impurities took place if the temperature was reduced below 900 K. Fig. 1 shows changes in the peaks peculiar to interstitial impurities on the Auger electron spectra. It is seen from Fig. 1 that the cooling of a sample leads to a considerable increase in the amount of impurities on the sample surface. Let us note once more that the quantitative data on the segregation of the samples made of industrial metals and specially prepared samples are similar and displayed in Table 1. Data in parentheses in Table 1 show that the impurities O, C and N segregate on the Y surface when the temperature is lowered. The further exposure of a sample for 10 and 20 min after the start of cooling revealed no increase in concentrations of impurities on the surface; this indicated that their segregation originated from near-to-surface layers to surface layers of a sample rather than adsorption of the components of residual gases under 1.5×10^{-7} Pa.

Because the segregation of impurities on a surface presupposes their accumulation in the near-to-surface

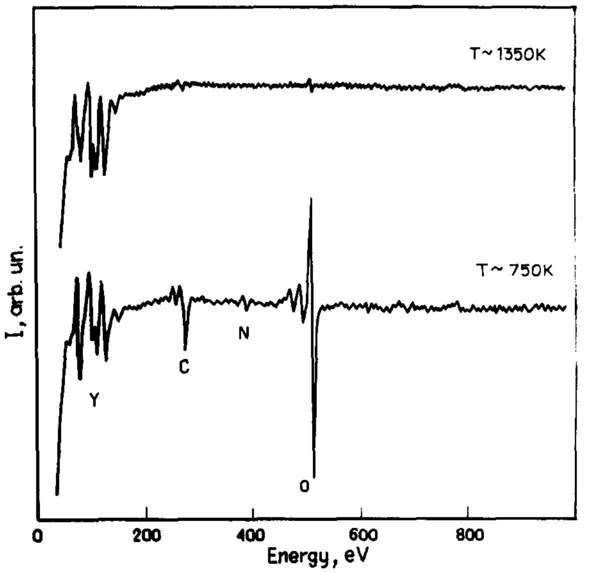

Fig. 1. Auger electron spectra of the yttrium surface during SSE at different temperatures: impurities segregation.

layers of a sample the problem of determining the depth of impurity concentration is of interest. The experimental geometry ruled out the possibility of ion etching in situ in the analytical chamber. Therefore the relevant part of a sample was placed in the preparation chamber of the electron spectrometer where layer-by-layer ion etching was performed followed by regular AES analyses of the surface. It turned out that the depth of yttrium enriched with O was about 1 μm (about 0.2 μm for C) at the anodic part of a sample which is most contaminated (Fig. 2). It should be noted that the depth was estimated rather roughly without taking into account possible "knocking on" effects, matrix and chemical effects, and probable formation of small particles of second phases (oxides, carbides etc.) when cooling the samples.

Since the nature of the segregation of O and C impurities is similar, all the further discussions and calculations are for oxygen as this is the most detrimental impurity to yttrium purification.

The following concepts of aging of metals and non-equilibrium and equilibrium surface segregations can elucidate the experimentally observed accumulation of the interstitial impurities on the surface of the yttrium when the latter is cooled. Let us consider probable mechanisms of impurity segregation.

3.1. Equilibrium surface segregation

This type of segregation is a well-known phenomenon which has been described in detail in Ref. [7]. It consists in the fact that the redistribution of surface-active impurities may lead to enriching structural inhomogeneities, at a free surface in particular, when the chemical potentials of dissolved impurities in an equilibrium system at a constant temperature are equal. The process of enrichment is energetically favourable because it decreases surface energy. Thicknesses of enriched layers can be several ångströms (about one monolayer) [8]. A layer approximately 1 μm thick is formed in our case (Fig. 2); therefore, equilibrium segregation alone cannot explain the fact observed experimentally.

3.2. Aging of metals

If the metal–impurity system contains the region for the presence of a solid solution then a threshold temperature exists for a particular concentration of an impurity. Nucleation of the second phase starts below this temperature. The growth of the second phase takes place over the entire volume of a sample including a free surface and other defects.

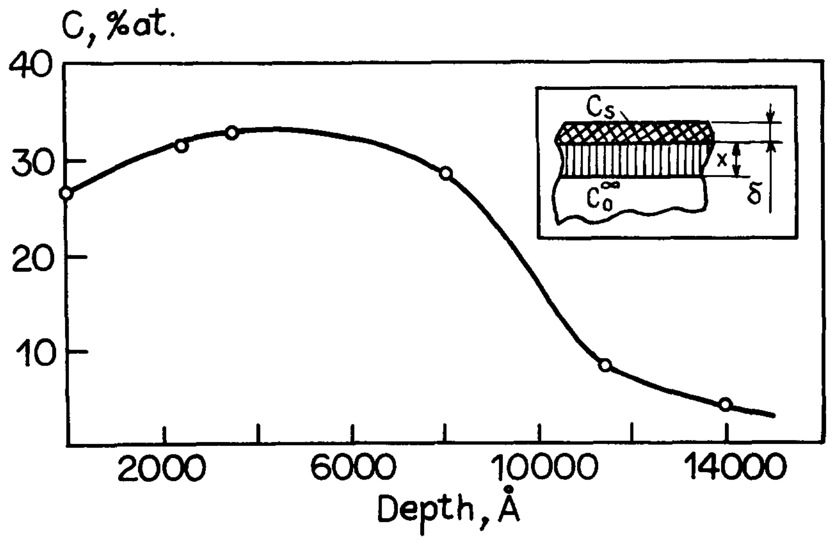

Fig. 2. The distribution of an oxygen yttrium over the depth of an enriched layer.

In the present case an increase in impurity concentrations, oxygen in particular, on the surface was observed on cooling from 1350 to 750 K. According to the diagram for the yttrium–oxygen state [9] the limit of oxygen dissolution in yttrium is 1 at.% at 500 °C. The bulk concentration of oxygen (0.34 at.%) in the specially prepared Y samples does not exceed this value. The content of oxygen in the industrial yttrium is 2.8 at.%. If even the excess oxygen is released as the second phase when the sample is cooled (this is hardly probable owing to the high rate of cooling, this being 250 °C min^{-1}) then the obtained value 1.8 at.% is considerably lower than that experimentally observed. Thus aging of metals is not the main reason for the accumulation of impurities on the surface.

3.3. Non-equilibrium surface segregation

Theoretically this question was considered in Refs. [7,8] and qualitatively it consisted in the following. At high temperature T_1 the equilibrium concentration C_1 of vacancies is high, being proportional to $\exp(-U_v/kT_1)$, where U_v is the vacancy formation energy. When the temperature is lowered to T_2 the concentration of vacancies decreases and tends to equilibrium $C_2 \propto \exp(-U_v/kT_2)$. The oversaturation $\Delta C_v = C_1 - C_2$ disappears at the drains, first of all at the free surface as well as on the grain boundaries and dislocations. Vacancies start flowing from the bulk to drains and to a free surface in particular. The vacancies capture impurities, the binding energy of which is more than kT, and transport them to a drain (surface). The binding energy of interstitial impurities with the vacancies in metals makes up, as a rule, several tens of electronvolts, which is sufficiently more than kT which is approximately 0.1 eV at 1300 K. Therefore oxygen, nitrogen and carbon can be referred to the class of impurities to which such a mechanism of segregation is most suitable. Disappearing at the drains (surface) the vacancies leave the zone with an increased concentration of impurities nearby which are not able to disperse kinetically at low temperatures. This results in the formation of a region of oversaturated solid solution where the occurrence of second phases can be expected. According to Ref. [8] such zones are of several fractions of a micron to 10–100 μm in size and they can be experimentally observed by various techniques in many metals on fast cooling and by annealing after exposure to radiation. The kinetic coefficient which determines the velocity of the movement of impurities to a drain with the flow of vacancies is supposed to be high, or at least not lower than the corresponding coefficient of heterodiffusion. Therefore the time required for the formation of concentrations C_i (with the bulk concentration C_v) on the Y surface can be estimated.

Let us consider the sample part adjacent to a surface (shown in Fig. 2) and introduce the following terms: C_i, the experimentally registered surface concentration of impurities after lowering the temperature from 1350 to 750 K; C_v, the equilibrium concentration of a dissolved impurity in α-Y at 1350 K; δ, the thickness of an enriched surface layer; $B = C_i/C_v$, the enrichment coefficient of a surface layer; x, the thickness of a "feeding" diffusion layer, the impurity of which is concentrated on a surface yielding the enrichment coefficient B; α, the lattice parameter of yttrium. It is easily seen that the thickness of the "feeding" diffusion layer is given by

$$x = (\delta/\alpha)\beta\alpha = \beta\delta$$

The time τ^* required to transfer the impurity from the "feeding" layer to enriched layer is of the order $\tau^* \approx x^2/D_v$, where D_v is the coefficient of the bulk diffusion of an impurity. Since the segregation effect is observed at cooling from 1350 K to 750 K the time τ^* should be estimated for the average temperature 1050 K.

The initial data for the calculation in the case of oxygen are as follows: $C_i = 27$ at.% (Table 1); $C_v = 0.34$ at.% (for the Y samples of higher purity); $\delta \approx 10^{-4}$ cm (Fig. 2); $D^{1050\text{ K}} = 6 \times 10^{-7}$ cm^{-1} s^{-1} [5]. The obtained value of the time (about 10^2 s) resulting from the estimation of impurity transport to a near-to-surface layer is in good agreement with the experiment in which the segregation is observed for the first 2 min after the start of cooling a sample. When using more contaminated industrial yttrium ($C_v = 2.8$ at.%) the time of transport becomes even less.

Let us estimate the concentration of vacancies and, consequently, the concentration which these vacancies provide for the enriched layer when moving to the surface. Metals with closely packed structures exhibit a relative concentration C of vacancies of order 10^{-1} at temperatures near the melting point. When all the vacancies diffuse from the feeding layer x to the enriched layer δ their concentration equals C. If we assume that $C = 5 \times 10^{-2}$ then C_δ is approximately 5 at.%, i.e. the flux of vacancies is less than the experimentally observed concentration of an O impurity, this being 27 at.%.

However, the investigated Y samples were polycrystals with a grain size of 10–15 μm for the industrially pure yttrium and 0.5–2 mm for the pure yttrium. In these samples the diffusion of interstitial impurities and their complexes with the vacancies can affect significantly the surface over the grain boundaries. The coefficient of grain boundary diffusion is much greater than that of bulk diffusion and their ratio varies mostly from 10^3 to 10^5 [7]. Under non-equilibrium conditions the accelerated diffusion favours the fast withdrawal of impurities and impurity–vacancy complexes through the grain boundaries to the surface from deeper layers. Dislocations play an analogous role. Thus all the above-mentioned mechanisms are likely to participate in the segregation of impurities to the surface. However, in our opinion, the main contribution comes from the non-equilibrium segregation including the transport of impurities and their complexes from the sample volume to the surface through the grain boundaries and dislocations.

Both the experimental discovery of the electron-stimulated diffusion of interstitial impurities on the Y surface in SSE and segregation of impurities revealed at the Y surface on cooling allowed the development of a method which permits more efficient and deep purification by electrotransport.

The method consists of solid phase electrotransport with regular cooling of the sample and removal of impurities segregating on a surface by the ion bombardments. When choosing a method of ion etching for such a highly active metal as yttrium special demands should be imposed on the purity of gases that are used for etching. It is worth noting that the partial pressure of chemically active components (O, C, N and H) must be minimized because the yttrium oxides, carbides and nitrides resulting from the ion bombardment have a rather low pressure of thermal dissociation up to the melting point and their removal by further annealing in ultrahigh vacuum becomes impossible.

From this standpoint the method of "triode" ion sputtering seems to be the most rational. According to this technique the Y sample, as the extremely negative Langmuir probe, is placed in low pressure gas discharge plasma. This permits ion bombardment of a sample surface, independent variation of such discharge parameters as gas pressure, current density, voltage and the production of a high density ion current onto a sample at low ion energies [10].

The inert gas that is used for ion etching must be highly pure and the partial pressure of chemically active impurities must be less than 10^{-7} Pa, that is it must be comparable with ultrahigh vacuum. Inert gas with a relative content of impurity gases of about 10^{-4} is sufficient for the use of a low pressure plasma (10^{-2}–10^{-4} Pa). To check the efficiency of this method the purification of yttrium by SSE with ion bombardment has been modelled. The scheme of this experimental modelling is presented in Fig. 3. Thermoelectronic cathodes were used to maintain the plasma in the region of low pressures. The electrons emitted by heated tungsten cathodes are accelerated to a grid anode which is positively charged (120 V). Oscillation near the grid prior to hitting electrons ionizes the process gas. Some of the formed ions move towards the negatively charged sample (2 kV) and bombard it, sputtering a certain layer.

The first model experiments have been carried out on Y samples with the residual resistance ratio $\gamma_{4.2} = 21$ using argon of 99.99% purity. The samples that were purified by SSE with ion etching (Fig. 4) became purer over the entire length that those treated without etching. In our opinion, purer argon and thorough cleaning of the construction materials of an ultrahigh vacuum system are required to minimize the generation of gaseous impurities on ion etching to achieve higher yttrium purity.

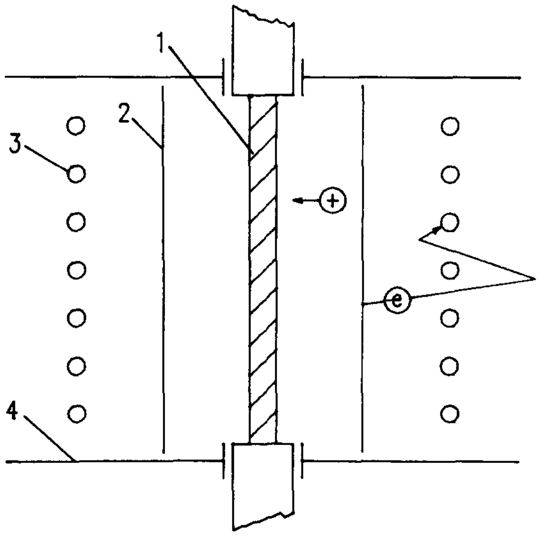

Fig. 3. The experimental scheme for SSE with ion etching: 1, Y sample; 2, thermocathodes; 3, grid anode; 4, screen.

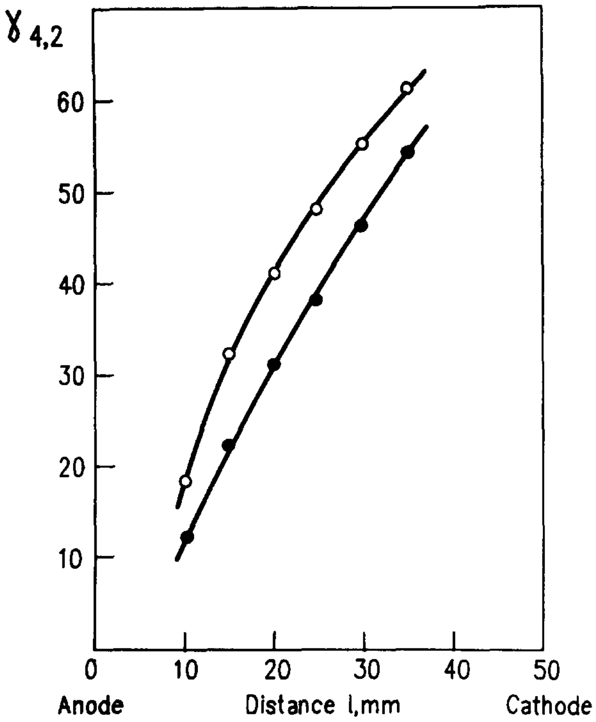

Fig. 4. The variation in the residual resistance ratio γ over sample length (equal SSE times): ●, after SSE; ○, after SSE with periodic cooling and ion etching (accuracy, 4%).

4. Conclusion

Investigation of the diffusion of interstitial impurities O, C, N on the surface of Y has been carried out by AES. It has been shown that degassing processes played a major role during the initial stage of purification by SSE. The behaviour of interstitial impurities has been revealed as correlative to that in the bulk. It has been experimentally found that below 900 K segregation of oxygen and carbon occurred to the surface of yttrium during electrotransport. Possible mechanisms for segregation are discussed with the conclusion that non-equilibrium segregation of interstitial impurities on cooling is most likely to be responsible mainly for this phenomenon. A method of purification of metals based on the combination of SSE with periodic cooling and ion etching of the surface is offered. Preliminary experiments displayed the possibility of using this method to make purification more efficient.

Further developments of this purification technique which may be of interest are the investigation of the influence of ion sputtering on purification efficiency and checking the possibility of alternative methods of ion sputtering, e.g. the Penning method.

Taking into account the importance of processes occurring on the surface of metals, investigations of phenomena taking place on the surfaces of metals by AES, X-ray photoelectron spectroscopy and secondary ion mass spectrometry at initially different concentrations of impurities and diffusion conditions are very promising.

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