Isotopic enrichment of metals in a pulsed electrotransfer process

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The phenomenon of isotopic enrichment of zinc has been observed in a process of pulsed electrotransfer during zone recrystallization of the material, and consists in the light isotopes (Zn^{64}) concentrating at that end of the material toward which the zone moved and to which the negative terminal of the current source was connected. On reversal of the current polarity, inversion of the effect and depletion in the light isotope were observed. Superimposing a direct current on the pulsed current intensified the effect. The isotopic-enrichment effect was intensified on increase of the pulsed-current frequency, of the strength of the current, and of the number of zone traverses.

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It is well known that in an electrotransfer process a material can be freed from impurities or a metal isotopically enriched as a result of the displacement of light isotopes in the direction of motion of the carriers[1-12].

However, the experiments carried out up to now have been set up using direct current only, although, from general physical arguments, it follows that a much greater effect can be achieved with the action of a pulsed current on the metal. The pulse technique has the following advantages. First, the nonstationary character of the passage of the current makes it possible to raise the current density from units to thousands of a/mm^2 (with a current-pulse duration of, e.g., $\sim 10^{-4}$ sec), i.e., by three orders of magnitude. Secondly, using high-voltage pulse capacitors, it is possible to raise the drift velocity of the electrons. Thirdly, the pinch effect, characteristic of a pulsed current (periodic contractions and expansions of the conductor with current in the radial direction by the intrinsic magnetic field), further stimulates diffusional separation of isotopes, in the same way as ultrasound acts on diffusion processes. Consequently, a pulsed current should intensify the pressure of the "electron wind" on the original natural mixture of isotopes in the metal and will facilitate the course of the separational diffusion processes.

The second technique which has been applied in the present work for purposes of isotopic enrichment of metals is to combine the action of a pulsed current with zone recrystallization of the material—the most common method of purifying a material[13]. In this case, on account of the repeated action of the zone, favorable conditions are created for maintaining and intensifying the isotopic enrichment of the metal attained in the separate stages of the process, and the ponderomotive forces of the current ensure agitation of the melt ahead of the crystallization front, and this reduces the thickness of the diffusion layer ahead of the crystallization front and should have a positive effect on the isotope-separation process.

The above advantages of the new technique enabled us in[14] to obtain isotopic enrichment of zinc in a shorter time than in the direct-current technique[3-12]. In the present work these investigations are continued. New results are obtained, which characterize the dependence of the effect on the frequency and magnitude of the pulsed current, on the polarity of the current, and also on the number of zone traverses and on the superimposition of currents of different forms. The distribution of the isotropic enrichment over the length of the material is found.

EXPERIMENTAL TECHNIQUES

The experiments were performed on zinc wires of length 300–350 mm and diameter ~1 mm, which were fitted into quartz tubes of diameter ~1.5 mm and placed in the zone-recrystallization apparatus (which is usually used for zone purification or for obtaining monocrystals). The setup is shown in Fig. 1. Helium was admitted into the space between the tube and the wire, creating a protective atmosphere. The ends of the wires were joined by electrical contacts to a pulsed-current source—a thyristor current modulator giving rectangular current pulses of duration $(30-150) \times 10^{-6}$ sec, frequency 0.2–2000 Hz and amplitude up to 2000 A. A direct current of strength up to 6 A was also used.

The zone recrystallization of the material was effected by means of a ring-heater oven, which moved on a trolley along the quartz tube with a velocity ~20 mm/min. The temperature in the oven channel amounted to ~550°C, which ensured the melting of a portion of wire approximately 6–7 mm long. In most of the experiments the wires were subjected to 20-fold action of the zone. Experiments were also carried out with up to 100 zone traverses. As a result of the repeated action of the zone end of the current, the original polycrystalline zinc wire was transformed into a monocrystal of the same length. After the experiment the long monocrystalline wire was cut into 15 mm lengths and, in this state, awaited mass-spectrometric and neutron-activation analysis. The operation of cutting the wire into lengths suitable for measurements of the isotopic enrichment made it possi-

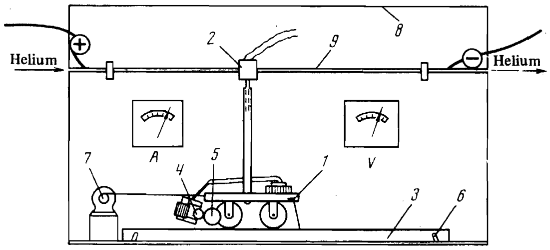

FIG. 1. Apparatus for isotopic enrichment of a metal in a process of pulsed electrotransfer and zone melting. 1–terminal switch; 2–oven; 3–rails for the trolley; 4–trolley drive; 5–reducing gear; 6–trolley stop; 7–trolley-return drive; 8–casing of the apparatus; 9–quartz tube with a wire of the metal being enriched.

ble to maintain the isotopic enrichment achieved in the metal for an unlimited time, since in this case diffusion processes could not return the metal to its original state.

The separate lengths of the wire (especially those from both its ends) were subjected to mass-spectrometric and neutron-activation analyses. The extent of the obtained isotopic enrichment of the metal and the distribution of the enrichment over the length of the wire were determined. The independence of the methods of measurement used guaranteed the accuracy of the analyses performed.

The mass-spectrometric measurements were carried out on an MS-1301 mass spectrometer, on the lines given by the isotopes with the masses of Zn^{64} and Zn^{68}. In natural zinc the content of these isotopes is such that the ratio of the lines for the corresponding masses should be 2.64 (Zn^{64}—48.895%; Zn^{68}—18.51%). In the mass-spectrometric measurements carried out, the change in the ratio Zn^{64}/Zn^{68} as compared with the natural ratio was determined. The spectra in the region of the masses 64 and 68 were run ~20 times for each sample. From these measurements the arithmetic-mean intensity of the lines mentioned was calculated. The error in the measurements amounted to ~1% of the original magnitude of the ratio Zn^{64}/Zn^{68}.

The neutron activation analysis was performed using the isotope Zn^{65}. Of all the zinc isotopes, only Zn^{65}, which is formed from Zn^{64}, has a large half-life and is very convenient for measurements. From the induced activity of the Zn^{65} we can estimate the Zn^{64} content in the samples. Cut lengths of wire of weight 0.04—0.08 g (the difference in weight for the same lengths of wire is explained by the mass transfer for different current polarities) were packed into quartz ampoules, sealed and sent for reactor irradiation.

The irradiation was carried out using thermal neutrons with flux density $\sim 1.2 \times 10^{13}$ n/cm^2·sec for one hour. After irradiation the samples were left for 1—2 weeks for the short-lived isotopes of possible impurities to decay. Besides the wire samples that had undergone the zone and current treatment, samples of the original zinc wire, in which the Zn^{64} content was the same as in natural zinc, were also irradiated. These original samples in each group sent for irradiation served as standards, and a comparison was made of the Zn^{65} content in the working samples with the Zn^{65} content in the standard samples.

The activity of the irradiated zinc was determined from the Zn^{65} photo-peak, having energy 1120 keV. In the measurements a spectrometer with a Ge(Li)-detector was used, and its resolving power with respect to the halfwidth of the Co^{60} photo-peak amounted to ~10 keV. An 800-channel LP-4840 analyzer made by the Finnish company "Nokia" was used as the amplitude analyzer. The error in the measurements was made up of the errors in maintaining the geometry in the measurements on different samples (the thickness and length of the samples and the positioning on the crystal) and the statistical errors in the counting. To reduce the first type of error calibration curves were taken for the original standard samples and the extent of the isotopic enrichment in the working samples was subsequently estimated from the difference in the activity of working and standard samples of a specific geometry and weight. Besides this, a comparison was made using the specific activity of the samples per mg. Starting from the experimental data, it can be seen that the total error in the measurements amounted to ~1.5% of the count given by the standard samples. The time of the measurements of the photo-peak from the radioactive samples was 1—3 min.

RESULTS

As was shown earlier [14], after several zone traverses, with simultaneous action of a pulsed current, a shift occurs in the isotopic ratio Zn^{64}/Zn^{68}, relative to the natural ratio, from 2.64 to 2.80 ± 0.03, which corresponds to an isotopic enrichment of approximately 6%. The light isotope Zn^{64} concentrates at that end of the wire which is connected to the negative terminal of the current source.

Figure 2a shows the dependence of the change in the ratio Zn^{64}/Zn^{68} on the number of zone traverses, from the data of the mass-spectrometric analysis, in percentages

$$\delta=\left[\left(\frac{Zn^{64}}{Zn^{68}}\right)_{\text{sample}} \Big/ \left(\frac{Zn^{64}}{Zn^{68}}\right)_{\text{stand}} - 1\right]\cdot 100,$$

and Fig. 2b shows the analogous dependence for the change in the concentration of the light isotope Zn^{64} from the activation-analysis data (ΔN is the increase in the photo-pulse count at the detector from the working samples; N is the pulse count from standard samples of the same geometry). The polarity of the current in both cases was favorable for enrichment in the light isotope at that end of the wire toward which the zone moved. Besides the pulsed current, a direct current of the same polarity and magnitude (with respect to the average value of the pulsed current) was also used. From the data presented it can be seen that the effect increases with increase in the number of zone traverses; the effect is also intensified when electric currents of different forms are superimposed.

Figure 3 shows the dependence of the change in concentration of the light isotope Zn^{64} on the frequency of the pulsed current, the polarity of the current, and its magnitude. The change in the average current (in the technique in which the frequency is varied at a constant current peak value I_p = 30 A) and in the current peak values (in the technique in which the frequency is varied at a constant average current value I_{av} = 1 A) are shown by additional scales. As can be seen from these data, as the frequency of the pulsed current increases, the magnitude of the effect increases, and changing from the favorable (+ → −) to the unfavorable (− → +) polarity of

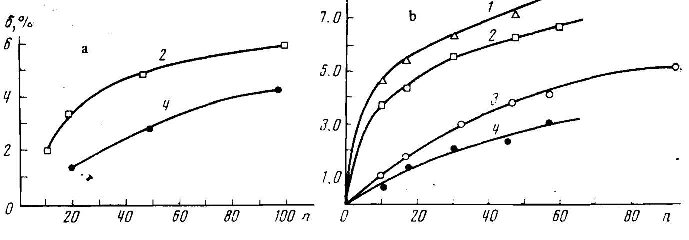

FIG. 2. Dependence on the number n of zone traverses of (a) the change in the isotopic ratio Zn^{64}/Zn^{68} from the data of the mass-spectrometric measurements, and (b) the change in the concentration of the light isotope Zn^{64} from the neutron-activation analysis data. Curve 1—pulsed and direct current I_{av} = 0.5 A; 2—pulsed current I_{av} = 0.5 A; I_p = 30 A; ν = 400 Hz; 3—direct current I_{dc} = 0.5 A; 4—without a current.

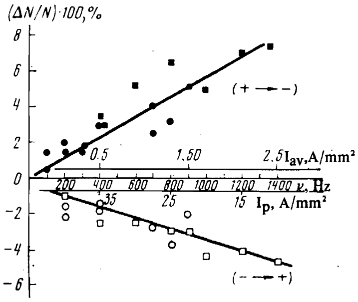

FIG. 3. Dependence of the change in concentration of the light isotope Zn^{64} (from the activation-analysis data) on the frequency and magnitude of the pulsed current, and also on the polarity of the current. ●,○ for $I_{av} = 0.2 - 1.8$ A; ■,□ for $I_p = 12 - 35.0$ A.

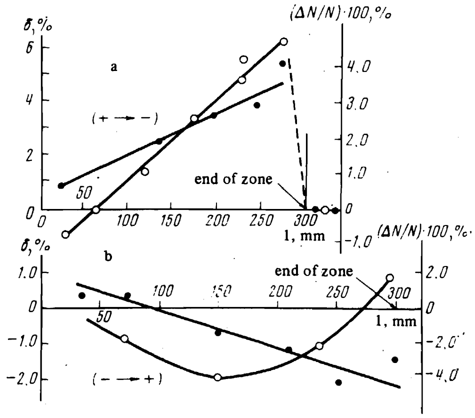

FIG. 4. Distribution of isotopic enrichment over the length of the zinc wire with favorable (a) and unfavorable (b) polarities of the current: a) $I_{av} = 1.62$ A; $I_p = 30$ A; $\nu = 900$ Hz; n = 17; b) $I_{av} = 0.5$ A; $I_p = 20$ A; $\nu = 400$ Hz; n = 20. ●–δ, %; ○–(ΔN/N) × 100, %.

the current (the arrow indicates the direction of motion of the zone) leads to inversion of the effect, i.e., in place of enrichment in the isotope Zn^{64}, depletion arises.

Figure 4 shows the distribution of the isotopic enrichment over the length of the wire for the favorable (a) and unfavorable (b) polarities of the current, from the data of the mass-spectrometric measurements (δ, %) and the activation analysis. Neither the enrichment (a) nor the depletion (b) in the isotope Zn^{64} is localized near the ends of the wire—they occupy regions of approximately ⅔ the length of the wire.

DISCUSSION OF THE RESULTS

Thus, in the recrystallization process, the light isotopes in zinc are displaced in the direction of motion of the zone, and the effect of the action of the zone is intensified as the number of zone traverses increases. This is a fundamental and important result, since this fact was not known from the theory and practice of zone melting[13]. Moreover, this agrees with the indications in the literature on the effect of the process of crystallization[15] and vaporization[16] on the isotopic composition of a material. It is known[13] that, if the impurity lowers the melting temperature of the material, in the process of zone recrystallization and purification its concentration becomes lower in the solidified part than in the liquid zone, and, therefore, the impurity is pushed back by the crystallization front and increases its content in the liquid phase and, consequently, in the end of the recrystallized material. It is easy to see the similarity between this type of behavior of impurities and that of light isotopic atoms. By virtue of the mass difference and the different diffusional mobilities associated with this, isotopic atoms can also affect the melting temperature of the material. For example, zinc consisting only of the Zn^{64} isotope, or tin consisting only of the Sn^{112} isotope, will possess a lower melting temperature. Therefore, it may be regarded as natural that the light isotope enriches the liquid phase in the process of recrystallization of the metal and increases its content in the end of the wire.

However, the recrystallization process creates only a small isotopic-enrichment effect (in our experiments, not greater than 3%) and the principal role in the proposed new method of isotopic enrichment of a metal belongs to the pulsed electrotransfer process. The zone recrystallization in the present case makes it possible merely to maintain and intensify the enrichment attained in the separate stages of the process. Indeed, as the narrow zone of molten metal moves along the original wire, under the conditions in which it is enriched by the light isotope (with the favorable polarity of the current), it serves as a place where, on the one hand, isotopic enrichment is constantly accumulated, and, on the other hand, the isotopic enrichment of the metal attained for a given number of traverses and for given regimes of action of the current is fixed by the trailing front of the zone (the crystallization front).

In the case when the negative terminal of the current source is connected to the end of the wire the effect reaches its maximum magnitude of 8–10%. But in the case when the positive terminal of the current source is connected to the end of the wire the effect is either absent (for small currents) or, conversely, depletion in the light isotope is observed, though not by more than 4–5% (for large currents and high frequencies), i.e., inversion of the effect occurs. But in this case (positive polarity at the end of the wire) a significant mass transfer of metal in the direction of motion of the zone was observed in our experiments. This may explain the anomalies, shown in Fig. 4b, in the behavior of the curves for the depletion in the isotope Zn^{64} over the length of the wires.

A change of regime in the passage of the pulsed current (for a constant peak value but different average value of the current, or for a constant average value but different peak values of the current) did not affect the extent of the isotopic enrichment of the metal, within the limits of the errors in the measurements.

Superimposing a direct current on the pulsed current leads to a further intensification of the effect, indicating the presence, and favorable influence in this case, of a constant component of "electron wind."

A comparison of the results of the measurements by the mass spectrometer (when the concentrations of the light and heavy isotopes are compared) and by the method of neutron activation analysis (which gives information of the concentration of the light isotope only) enables us to conclude that during pulsed electrotransfer it is mainly the light isotopic atoms Zn^{64} that are transferred in the process of zone recrystallization of the material.

Unlike impurities, which, in the zone melting process, concentrate at the end of the wire over approximately ⅓ the length[13], light isotopic atoms are increased (or depleted) in content over approximately ⅔ of the length of the wire, and therefore the similarity in the behavior of isotopic and impurity atoms is only superficial.

To estimate the isotopic enrichment we use the usual criterion $\mu = \alpha\overline{M}/\Delta M$, called the mass effect ($\alpha = \Delta U_{eff}/U_{eff}$ is the relative difference in the effective mobilities of the ions; $\overline{M}$ is the mean mass of the ions, and $\Delta M = M_1 - M_2$ is the mass difference between the isotopic ions). Since, in a liquid metal, according to[1], we must expect $\mu = 0.1 Z_{\text{eff}}$ (Z_{eff} is the effective charge of the ion), and Z_{eff} for an activated ion is equal to several units, the mass effect should be equal to several tenths. The experimental values for μ for different metals lie in the range of values 0.06–0.25[1].

To estimate the mass effect in our experiments, we replace the five-component mixture of isotopes in zinc by a model two-component mixture. We shall assume that the mean degree of enrichment of one half of the wire relative to the other is $(\Delta N/N) \times 100 = 5\%$, and that the mean difference in the mass numbers is $\Delta M = 4$. The transfer of the light component (Zn^{64}) across the center of the melting zone in time t is, in accordance with the theory of Bresler and Pikus[9],

$$Q' = E\Delta U_{\text{eff}} c_0 (1 - c_0) nts$$

(s is the cross-section of the wire; ΔU_{eff} is the difference in the ion mobilities; c_0 is the initial concentration of the light isotope: $c_0 = 0.5$; t is the total time of action of the current over a length of wire corresponding to the zone length ~7 mm and is equal to $t = nl/v$, where n is the number of zone traverses and v is the speed of motion of the zone, equal to 20 mm/min, i.e., $t = 20 \times (7/20) \times 60 = 420$ sec). We replace E by $\rho I/s$ (I is the average current across the zone and ρ is the resistivity of the metal); then

$$Q' = I\rho\Delta U_{\text{eff}} c_0 (1 - c_0) nt.$$

We introduce into the latter formula a coefficient $K_1 > 1$ proportional to the number of zone traverses, i.e.,

$$Q = I\rho\Delta U_{\text{eff}} c_0 (1 - c_0) ntK_1.$$

On the other hand, the accumulation of the heavy component in the left part of the zone is expressed by the formula

$$Q'' = (m/2\delta) n\Delta c,$$

where m is the weight of the metal and δ is its specific gravity. We also introduce into this formula a coefficient $K_2 > 1$ proportional to the number of zone traverses:

$$Q = (m/2\delta) n\Delta c K_2.$$

Equating the two expressions for Q, we obtain

$$I\rho\Delta U_{\text{eff}} c_0 (1 - c_0) ntK_1 = \frac{m}{2\delta} n\Delta c K_2.$$

Hence we obtain an expression for the difference in the mobilities of the light and heavy isotopic components in our experiments:

$$\Delta U_{\text{eff}} = \frac{m}{2\delta} \frac{\Delta c}{c_0} \frac{1}{(1 - c_0)} \frac{1}{I\rho t} \frac{K_2}{K_1}.$$

Substituting into this the numerical values $\Delta c/c_0 = 0.05$, $(1 - c_0) = 0.5$, $I = 0.5$ A, $t = 420$ sec, $\rho = 1.2 \times 10^{-5}$ ohm·cm, $\delta = 7.14$ g/cm^3 and $m = 1.93$ g (the mass of the metal being enriched), and putting $K_1 \approx K_2$ as a first approximation, we obtain $\Delta U_{\text{eff}} = 5.3$ cm^2/V·sec.

The usual Einstein mobility of ions in a zinc melt can be calculated from the relation $U_{\text{eff}} = DEe/kT$ (D is the self-diffusion coefficient in liquid zinc, equal approximately to 1.55×10^{-5} cm^2/sec, E is the magnitude of the field, equal to 0.765×10^{-3} V/cm, and e is the electron charge). Substitution of the numerical values gives the ion mobility $U_{\text{eff}} = 4.1 \times 10^2$ cm^2/V·sec. Thus, the mass effect μ in our experiments was approximately equal to

$$\frac{\Delta U_{\text{eff}}}{U_{\text{eff}}} \Big/ \frac{\Delta M}{M} = 0.21.$$

The value found corresponds to the maximum values of μ from the data of[1,2] for other metals with direct current.

It may be conjectured that it will also be possible to obtain more effective purification of an electrically conducting material by the method described than by ordinary zone melting or by a combination of the latter with direct-current electrotransfer.

CONCLUSIONS

Thus, during pulsed electrotransfer and zone melting, isotopic enrichment of the metal occurs, and intensifies with increase of the frequency and amplitude of the pulsed current, and also with increase in the number of zone traverses. Superimposing the action of a pulsed and a direct current intensifies the isotopic-enrichment effect. The light isotope concentrates in the region of the negative terminal of the current source. The enriched regions occupy approximately ⅔ of the original material, i.e., the effect has a volume character. In the case of interchange of the current polarity, inversion of the effect occurs, and instead of enrichment, depletion with respect to the light isotope occurs (with an approximately equivalent enrichment in the heavy isotope).

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