

Preparation of high purity tellurium by zone refining

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Abstract. This paper describes purification process of tellurium metal using zone refining technique under high purity hydrogen gas ambient in normal room environment. Process automation by newly designed stepper motor drive and allied process control instruments circumvent the complexity of electrical motors. It is observed that overall impurities have gone down substantially from 4N+ to 5N5 purity with reference to Fe, Mg, Al, Cr, Zn, Bi and Cu. Removal of selenium is effected by hydrogen, which also serves as carrier gas during zone refining. The selenium in tellurium matrix is found to be below detection limits. The zone temperature, zone length and tilt angle maintained in the experiment are adequate to go down to high purity levels.

Keywords. High purity tellurium; zone refining; selenium.

1. Introduction

Ultra pure tellurium (Te) metal has become an important metal in opto-electronic applications over the last couple of decades for fabricating high performance infrared devices for thermal imaging and night vision cameras. The required purity of input material for the above mentioned devices is 6N and above so as to obtain a fewer than 10^{15} carriers/cm³ in mercury cadmium telluride (MCT) substrates (Fricke Jr. and Riechard 1978; Burd *et al* 1980). The unwanted impurity concentrations create deep energy levels in the energy gap. Also, the carrier mobility, which depends on the scattering mechanisms, is a function of crystal perfection and purity (Willardson and Beer 1981). Therefore, careful attention has to be paid to purification procedures and greater care should be taken to analyse their ppb/ppm level impurity concentrations.

Techniques of zone melting developed (Pfann 1952) are soon going to be half a century old. The tremendous progress made in applications of zone melting techniques (Pfann 1966) is not only on account of its being a powerful purification technique, but also, because of its simplicity in operation. Literature survey (Schumacher 1953; Handley and Herington 1956a,b; Rock 1956; Ronald 1959; Beynon and Saunders 1960; Herington 1960; Wilman 1961; Sloan and McGowen 1963; Zief *et al* 1963; Knypl and Zielenski 1963; Singh *et al* 1968; Singh 1973, 1976) reveals that dual electric motors are used for different forward and backward speeds for reciprocating movement of the heaters. Such a drive mechanism essentially

envisages the mechanical disengagement of the slow drive motor and engagement of the rapid reversing motor.

Owing to relatively medium range melting point (449.50°C) and thermal conductivity, as also majority of the impurities having suitable segregation coefficients (much less than one), multi zone refining and gradient crystallization with removal of end material is used as an effective refining process (Capper 1982; Kuchar *et al* 1996). It is reported that the cadmium metal is purified up to 6N and above by quadruple zone refining under hydrogen atmosphere (Mathur and Singh 1989). The attempts to refine indigenous tellurium by zone refining have shown that not much literature is available on ultra pure tellurium purification processes (Mungekar *et al* 1973). In the country, except the Bhabha Atomic Research Centre (BARC), no other laboratory has made efforts to purify the electronic metals up to 6N and above, which may be due to substantial investment required for infra-structural, process and analytical facilities. On the other hand, it is difficult and expensive to import ultra pure tellurium due to its strategic nature. In view of the above, systematic efforts have been made to create infrastructure, indigenous process equipment and developed methods to analyse the purified material. The zone refining experiments on 4N tellurium in a quartz tube of GE214 grade under moisture free and pure hydrogen gas ambient in the normal environmental conditions have been carried out to find out the extent of expensive clean room requirement. The results obtained so far are discussed in this paper.

2. Experimental

The present automatic horizontal zone melter designed and fabricated from locally available components with

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microprocessor-controlled stepper motor renders the fabrication of the drive mechanism not only simple but also compact and elegant. The technical details of the microprocessor controlled stepper motor drive are being published elsewhere. This horizontal zone refiner is with four heaters of ~ 1 kW and the zone width controlled by "Maxthermo" make PID temperature controllers with an accuracy of $\pm 1^\circ\text{C}$. The horizontal, forward as well as reverse motions were controlled by a stepper motor of 24 V and 1.6 A capacity. The entire system was controlled by a programmable microprocessor. The picture of the zone refining system along with accessories is given in figure 1. The salient features of the system are as follows. A quartz tube of 1630 mm long and 55 mm diameter was connected using stainless steel flanges to a "Domnick Hunter make" hydrogen generator of capacity ~ 160 cc/min along with necessary molecular sieves.

The GE 214 grade quartz material was used to make a boat of 560 mm long and ~ 25 mm diameter and 20 mm height and a thickness of ~ 2 mm. As received tellurium (4N pure) chunks of weight 500 g was loaded into quartz boat and melted in a furnace under hydrogen atmosphere to get horizontal and uniform melt bar of tellurium. Figure 2 shows the molten melt in a quartz boat. The boat along with tellurium melt was then loaded into the zone refiner having a tilt angle of $\sim 2^\circ$ to avoid mass transfer during zone refining. The microprocessor was programmed for 15 passes (one cycle) and the temperature of all the zones were maintained at $480 \pm 1^\circ\text{C}$ using K-type sensor and PID temperature controllers. The zone length at the temperature was around ~ 6.7 cm. The speed of stepper motor was set at 3 cm/h and the zone refining experiment was carried out under continuous hydrogen gas flow. The hydrogen selenide produced during reac-

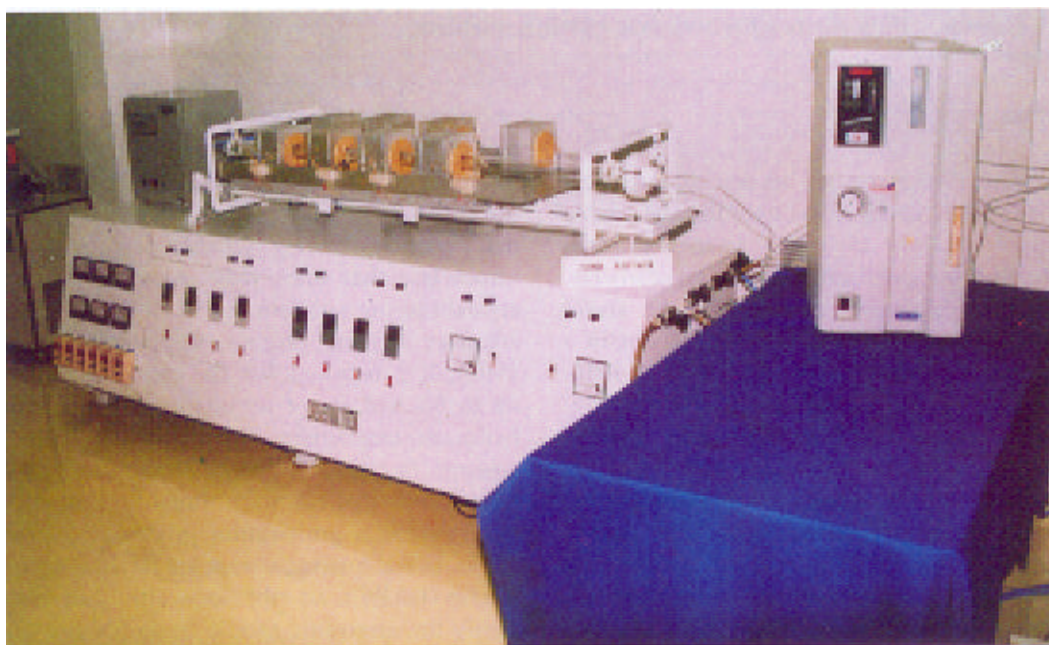


Figure 1. Indigenous automated resistive zone refiner set up.

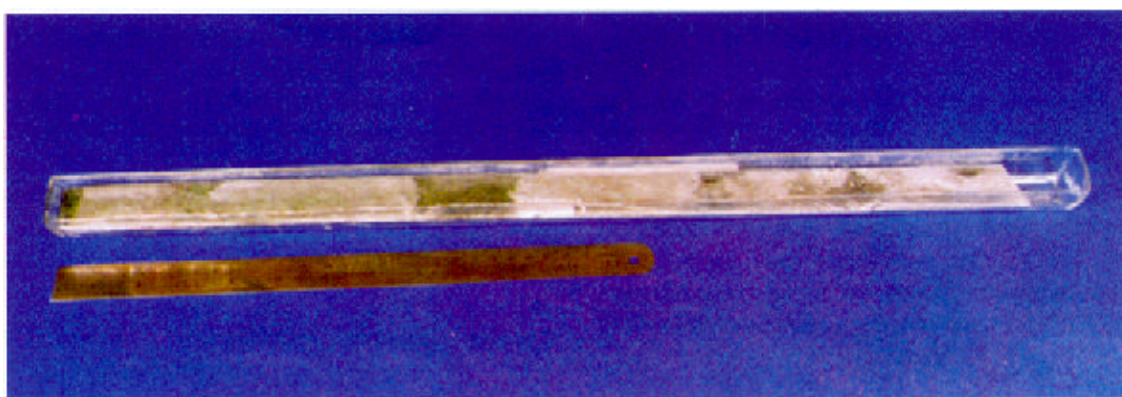


Figure 2. Quartz boat containing uniform melt of 4N tellurium. The last portion in the metal bar is cut for analysis.

tion was neutralized before letting it out into the atmosphere. In a single batch, four cycles were completed and at the end of each cycle, the zone-refined ingot was cut into three portions, viz. right end portion (~ 70 mm), middle portion (~ 420 mm) and left end portion (~ 70 mm). The middle portion was again melted in a cleaned and separate quartz boat to get a homogenized bar and then continued the zone refining experiment for cycle 2. Similarly experiments for cycles 3 and 4 were carried out.

During the initial stages of experiment, the IOLAR grade hydrogen gas supplied through cylinders was used to create ambient flow. Due to this, black and amorphous powder was formed on the tellurium metal bar, which could be due to reaction of moisture from the hydrogen cylinder on the tellurium metal bar. However, it disappeared when the hydrogen gas from the hydrogen generator was used indicating the essence of high purity hydrogen gas (~ 7N pure) while doing such experiments.

3. Analytical procedure

The samples along the length of the ingot each weighing 2 g were taken and powdered, dissolved in 50% supra-pure HNO_3 in a teflon beaker. The supernatant liquid was transferred after series of washings into a 25 ml volumetric flask. The solution was then analysed using inductively coupled plasma optical emission spectrophotometer (ICP-OES). The reproduced results were plotted to see the segregation of impurities.

4. Results and discussion

The results have been studied for most prominent impurities such as Fe, Mg, Al, Cr, Zn, Bi and Cu. It is

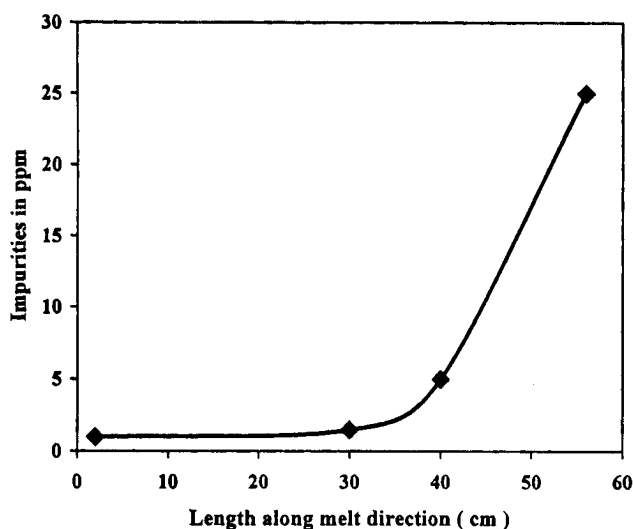


Figure 3. Typical curve representing impurity segregation in tellurium matrix (Willardson and Beer 1981).

observed that most of the impurities have gone below detection limits except Fe, Al, and Mg, which were present in increasing order. These are attributed to be due to the effect of environment. The reduction of impurities in the solute after passing through a single molten zone of length, l through a homogeneous solid ingot of length, L is given by the equation

$$C_x/C_0 = 1 - (1-K)e^{-Kx/l},$$

where C_x is the solute concentration at a distance x at the freezing solid-liquid interface and C_0 the initial uniform solute concentration and K the segregation coefficient defined as the ratio of solute concentration in the solid to the melt at the crystallization interface. Practically, it requires large number of zone passes (each pass is about 8 h) to reach ultimate distribution. However, after certain number of passes (say 15), it is expected that the segregation becomes negligible and hence it is presumed that the UD is almost reached. In order to further purify the material, the middle portion (~ 70%) is again melted to distribute the impurities uniformly in the entire ingot length (560 mm in the present case). By repeating this three or four times, it is expected that the impurities should be segregated to the maximum extent.

Table 1 shows the ICP-OES analytical data for the trace impurities present in the right, middle and left portions for all the four cycles. It is clearly seen that except Fe, Al and Mg, most of the impurities have gone below detection limits in the middle region which is expected to be the purer one. The typical curve for the segregation of impurities in tellurium matrix is given in figure 3 (Willardson and Beer 1981). The experimental results of the elements for which the detection limits are higher are divided into two categories, depending on the value of impurity segregated at the end of the ingot and plotted in figures 4 and 5. It is clear from these two

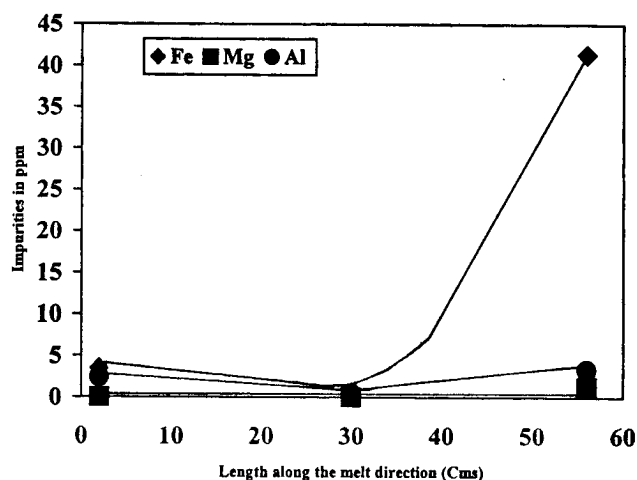


Figure 4. Segregation of Fe, Mg and Al impurities along the length of zone refined tellurium ingot.

Table 1. ICP-OES data for zone refined tellurium.

Element	Starting material	Initial region No. of cycles				Middle region No. of cycles				End region No. of cycles			
		1	2	3	4*	1	2	3	4*	1	2	3	4
Cr	0.57	0.5	< 0.05	< 0.05	< 0.05	0.1	0.13	< 0.05	< 0.05	0.13	0.07	< 0.05	4.53
Zn	0.1	0.1	0.25	< 0.01	< 0.01	0.1	0.42	< 0.01	< 0.01	0.1	0.37	0.72	0.12
Cd	0.1	0.1	< 0.01	< 0.01	< 0.01	0.1	< 0.01	0.03	< 0.01	0.1	< 0.01	< 0.01	< 0.01
Pb	4	0.5	0.5	< 0.1	< 0.1	0.5	< 0.1	< 0.1	< 0.1	15.5	0.62	< 0.1	< 0.1
Bi	2.3	0.5	< 0.1	< 0.1	< 0.1	0.4	0.56	0.18	< 0.1	4.8	0.56	0.27	< 0.1
Cu	1	0.5	0.04	0.14	< 0.01	0.1	0.1	0.06	< 0.01	4.2	0.15	0.02	0.28
Co	0.1	0.1	0.1	< 0.02	< 0.02	0.1	0.1	< 0.02	< 0.02	0.5	0.1	< 0.02	< 0.02
Ni	1.25	0.1	0.1	0.08	0.13	0.25	0.38	< 0.05	< 0.05	5.75	0.1	0.04	< 0.05
Fe	14	0.1	1.68	< 0.02	3.45	1.0	2.4	0.18	0.62	5.8	1.6	0.12	41.4
Mn	0.07	0.05	0.03	< 0.01	< 0.01	0.07	0.05	< 0.01	< 0.01	0.05	0.04	0.06	0.29
Mg	0.33	1	0.5	< 0.01	< 0.01	0.58	1.3	0.2	0.05	0.46	0.32	1.08	0.88
Al	1.2	0.7	0.8	0.77	2.42	2.58	0.9	0.69	0.55	2.3	0.9	3.2	3.38

*Pure tellurium material part in the zone refined bar. (All values in ppm).

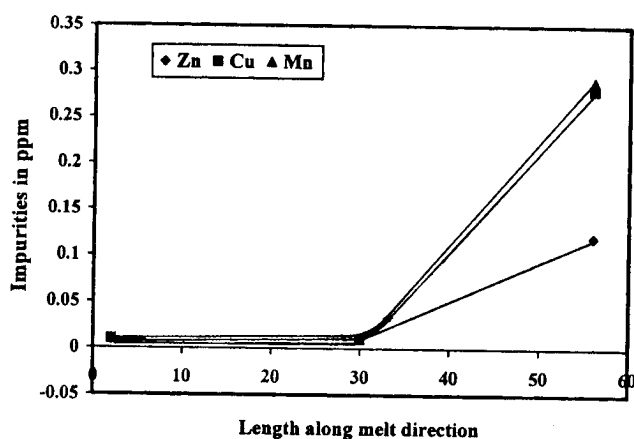


Figure 5. Segregation of Zn, Cu and Mn impurities along the length of zone refined tellurium ingot.

figures that the segregation behaviour very nearly matches with the typical impurities segregation curve shown in figure 3. The curves in figures 4 and 5 indicate that the control point is somewhere at 30 cm distance for Fe, Cu and Mn from the beginning of the metal bar and is expected to increase towards right side with the increase in number of cycles as also by taking more number of samples (say for every 2 to 3 cm) towards the right end of the metal ingot and analysing the impurities and plotting. However, the curve shape more or less remains the same. The analytical result in table 1 implies that the 5N+ purity is achieved barring the impurities Fe, Al, Mg. The samples should invariably be analysed using mass spectroscopic techniques such as ICP-MS and glow discharge mass spectrometer (GD-MS) to estimate ppb/ppt level impurities. The selenium whose segregation coefficient is nearer to one in Te matrix was actually around 18 ppm in the raw material and has ultimately reduced to below detection limits after second cycle indicating the

reaction of hydrogen on the selenium forming hydrogen selenide vapours and got carried away along with high flow rate of hydrogen gas. The analysis of sodium hydroxide solution has actually shown an increase in the quantity of selenium at the end of the experiment indicating the effective selenium removal during zone refining itself. The results of selenium were doubly confirmed by two other techniques, viz. ICP-MS and Graphite furnace atomic absorption spectrometer GFAAS (which were done at different laboratory facilities).

5. Conclusions

From this study the following conclusions are drawn. Process automation by newly designed stepper motor drive and allied process control instruments circumvent the complexity of electrical motors. Clean room ambience appears mandatory to reduce Fe, Al and Mg impurities in zone refining. Separate experiment to remove selenium may not be required as the removal of selenium impurity in tellurium matrix by hydrogen gas flow during zone refining is effective, provided the selenium quantity is around 18 ppm in the raw tellurium. The purity of hydrogen is very important (around 7N) for zone refining of tellurium to achieve high purity.

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