

FINAL REPORT
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CHEMICAL COMPATIBILITY OF CARTRIDGE MATERIALS

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A. OBJECTIVE

The objectives of this study were to determine the chemical compatibility of TZM with GaAs and CdZnTe, and Inconel with HgCdTe and HgZnTe. At the present time no other studies regarding the compatibility of these crystal components and their respective cartridge materials have been performed. This study was to identify any possible problems between these materials to insure proper containment of possibly hazardous fumes during crystal growth experiments. In this investigation the reaction zone between the materials was studied and the amount of degradation to the system was measured.

B. EXPERIMENTAL PROCEDURE

Bulk cartridge capsules were made in the configuration shown in Fig. 1. The cartridge material was either TZM, WC103, or Inconel. The original radius of the hole was measured and the capsule loaded with its respective semiconductor material and plugged. In the case of TZM and WC103 a molybdenum plug was used. Each loaded cartridge container was subjected to a heat treatment in a horizontal tube furnace. The heat treating atmosphere was flowing argon. The heat treating cycle was dependent on the semiconductor material and was conducted according to the heat treatments prescribed by NASA. These cycles will be

described during the discussion of each semiconductor/cartridge material system.

After heat treatment, the samples were sectioned normal to the cylindrical axis revealing the semiconductor-cartridge interface as a circle. The samples were then polished and etched to better distinguish reacted and unreacted zones. The radius of the circular interface between the reaction zone and unreacted base metal was measured. The technique used involved measuring 10 points around the circumference of the reacted zone. The radius was then determined by a series of 10 sets of three simultaneous equations and averaging the results. The results are valid with the assumption that the reaction between semiconductor and base metal was uniform around the surface of the cylinder. The samples were examined using a Scanning Electron Microscope (SEM) and elemental analysis of the zones present were determined using Energy Dispersive X-Ray Analysis (EDX).

C. SYSTEMS AND RESULTS

1. TZM with GaAs

a) Heat treatment - The heat treating cycle was designed to be as close to that specified for GaAs (Fig 2). This cycle consisted of heating from 50°C to 1260°C in 4.2 hrs or a rate of 4.8°C per minute. The temperature was held at

1260°C for varying times. Then cooled from 1260°C to 160°C in 9.71 hrs or at a rate of 2°C per minute. Hold times used were 0.0 hrs, 9.63 hrs, 14.8 hrs, 20.63 hrs, and 26.63 hrs. The total heat treatment times ranged from 13.3 hrs to 40.0 hrs. The desired total heat treatment time of importance to NASA was 28.17 hrs. The weight of GaAs used in each sample averaged 311 mg.

b) Radius measurements - The average radius results for the TZM/GaAs samples run are shown in Table 1. Samples MG32, MG7, and M68 were run previous to the discussed procedure thus the original cylinder radius is an average of the measured values, under the assumption that there were no major differences in machined capsules. The reaction depths, determined by subtracting the original radius from the reacted radius, range from 0.0765 mm to 0.1494 mm. The percentages indicated are the reaction depths divided by the designed cartridge thickness of 0.6858 mm (0.027 in) and multiplied by 100. The penetration of the GaAs into the TZM after the desired heat treatment of 28.17 hrs was 0.1152 mm or 16.8% of the desired cartridge thickness. These percentages indicate that the TZM cartridge could withstand exposure to GaAs without a great loss in thickness.

c) SEM and EDX - Figure 3 shows the typical appearance of a cross-sectioned TZM/GaAs sample. The overall appearance of the cross-section indicated a definite reaction between TZM and GaAs. Figure 4 shows the appearance of the reaction

zone/base metal interface at a higher magnification. At the reacted/unreacted base metal interface different zones were present as indicated by EDX examination. At point 1 in Figure 4, both gallium and arsenic were present in small amounts along with molybdenum from the TZM base metal. At point 2, arsenic and molybdenum were seen but gallium was not found. Point 3 contained a high concentration of gallium with molybdenum and at point 4 there was a strong indication of gallium compared to molybdenum. Some arsenic also was present at point 4. The dark grey area was unreacted GaAs.

2. WC103 with GaAs

a) Heat Treatment - Heat treating times and temperatures for WC103 and GaAs were the same as those described for TZM and GaAs. Samples for the WC103 series were heat treated along with the TZM series. The heat treating time of interest for crystal growth experiments was the 28.17 hrs total time.

b) Radius measurements - The results of the radius measurements for WC103 and GaAs are shown in Table 2.

Reaction depth measurements range from 0.4671 mm to 0.6050 mm which corresponded to 68% to 88% loss in cartridge integrity. The values in this study fail to increase with increasing heat treatment times due to the fact that the amount of GaAs used in each sample was not sufficient to provide an infinite source to react with the WC103. Further

investigation of this system will involve modifications to the capsule dimensions to overcome this problem. The results show that the reaction between WC103 and GaAs was very severe. Due to greater amounts of GaAs involved in the proposed crystal growth experiments, the use of WC103 as a cartridge material is not advisable.

c) SEM and EDX- The typical appearance of a cross-sectioned WC103/GaAs sample is shown in Figure 9. The reaction zone thickness was considerably greater than that seen for TZM and GaAs. Figure 10 shows the reacted area/base metal interface. The WC103 base metal was the lighter grey area shown on the right side of the photo. EDX analysis showed gallium present at the reaction zone interface. An increase in gallium concentration was observed from point 1 to point 2 (Figure 10). The area of increased voids corresponded to an increase in arsenic concentration with a decrease in gallium concentration. EDX at point 3 indicated only a small amount of gallium present with strong arsenic and niobium peaks. EDX scans for points 1, 2, and 3 are shown in Figures 11, 12, and 13 respectively. Distinctions between gallium rich and arsenic rich zones was observed in all WC103/GaAs samples. The one difference between samples observed was that the width of the gallium rich layer decreased with increased heat treating times. In all samples no unreacted GaAs was found.

3. WC103 with CdZnTe

a) Heat treatment - The heat treatment cycle for WC103 and CdZnTe was as follows. The samples were heated from 50°C to 1170°C in 9.8 hrs (2°C per minute). Samples were held at 1170°C for 0.0 hrs, 11.0 hrs, 41.0 hrs, and 77.42 hrs. The samples were cooled from 1170°C to 170°C in 9.17 hrs (1.8°C per minute). Total heating times range from 19 hrs to 96.67 hrs. The time of interest for the crystal growth experiments was 96.67 hrs. The weight of CdZnTe used averaged 357 mg per run.

b) Radius measurements - The results of radius measurements for the WC103/CdZnTe series are listed in Table 3. The samples seem to follow a trend with the rate of CdZnTe penetration into the WC103 being 0.00146 mm/hr as shown by the plotted data in Figure 14. The penetration depth at 96.67 hrs was 0.2165 mm(31%) of the designed cartridge thickness. The reaction depths calculated correspond to 15% to 31% of the designed cartridge thickness. For CdZnTe, the use of the niobium alloy, WC103, as a cartridge material appears to be acceptable. A corresponding loss in strength properties with degradation may present a problem.

c) SEM and EDX - Figure 15 shows the typical appearance of the WC103/CdZnTe sample cross-section. This figure shows the large amount of unreacted CdZnTe remaining in the capsule. The layer at the reacted/unreacted base metal

interface is shown in Figure 16. The unreacted base metal is to the left with the unreacted CdZnTe to the right. Grains such as the one indicated in Figure 16 as point 1 and those which appear closer to the interface contain Nb and Te (EDX, Fig.17). The areas indicated by points 2 and 3 are unreacted CdZnTe. In this system, Te seemed to be the leading contributor to the attack on WC103.

4. TZM with CdZnTe

a) Heat treatment - The heat treatment for the TZM/CdZnTe system was identical to that described for the WC103/CdZnTe system.

b) Radius measurements - Radius measurements as shown in Table 4 were inconclusive due to the fact that the containment of the CdZnTe at 1170°C was not achieved. The time of reaction between CdZnTe and the capsule before the CdZnTe escaped into the furnace atmosphere could not be determined. The sample capsule has been redesigned for this system and sample preparation is included in future work.

5. Inconel and HgCdTe

a) Heat treatment - A total of 5 samples were run for the Inconel/HgCdTe system. The samples were heated from 25°C to 625°C in 2.9 hrs (3.5°C per minute). Samples were held at 625°C for 0.0, 1.6, 3.1, 5.25, and 9.6 hrs. Samples were then cooled from 625°C to 150°C in 7.5 hrs (1°C per minute).

Total heat treatment times were 10.4, 12, 13.5, 15.65, and 20.0 hrs for respective samples with the time of interest being 15.65 hrs. The heat treating atmosphere was flowing argon. The average weight of HgCdTe used in the capsules was 660 mg.

b) Radius measurements - The result of radius measurements of the Inconel/HgCdTe samples and reaction depths are shown in Table 5. The reaction occurred at a rate of approximately 0.00701 mm/hr. Reaction depths ranged from 0.0483 mm to 0.1168 mm for the total heat treatment times of 10.4 hrs and 20.0 hrs respectively. The depth measured for the 15.65 hr. run was 0.1118 mm. Measurements corresponded to a 7% to 17% degradation in the designed cartridge thickness. The results are plotted in Figure 18. Due to the lower temperature and times in the Inconel/HgCdTe series, Inconel should be an acceptable cartridge material for HgCdTe.

c) SEM and EDS - The reacted area in a typical Inconel/HgCdTe sample is shown in Figure 19. The area contained two distinct zones, the first being at the unreacted base metal interface. This was a thin zone which continued around the circumference of the reaction cylinder. EDX at point 1 showed strong indication of the presence of Te, along with Cr and Mo from the Inconel base metal. At point 2 a strong Te peak with small Ni and Cr peaks were present with an absence of Mo. The areas denoted by point 2

and 3 made up the second zone in the reacted area. At point 2, Te, Cr, and Ni were present and at point 3 Hg, Cd, and Te were present. In sample IC1, only the first zone was present. The unreacted HgCdTe started at point 4. EDS scans for points 1-3 are shown in Figures 20-22 respectively.

D. FUTURE WORK

Future work will consist of the reevaluation of the TZM/CdZnTe system and the study of Inconel/HgZnTe compatibility. The diffusion mechanisms and theoretical rates which apply to the systems compatibility will be determined.

Table 1. TZM and GaAs compatibility data

Sample #	Base/Semi-conductor Material	Total Heat Treatment Time (hrs)	Original Cylinder Radius(mm)	Reacted Radius (mm)	Reaction Depth mm (%)
MG01	TZM/GaAs	13.31	2.7432	2.8197	0.0765 (11.15)
MG4	TZM/GaAs	18.0	2.7432	2.8850	0.1418 (20.68)
MG5	TZM/GaAs	23.0	2.7686	2.8689	0.1003 (14.63)
MG32	TZM/GaAs	28.17	2.7517*	2.8669	0.1152 (16.8)
MG7	TZM/GaAs	34.0	2.7517*	2.9011	0.1494 (21.78)
MG8	TZM/GaAs	40.0	2.7517*	2.8381	0.0864 (12.6)

Note: Original Radius (mm) * - Average of measured values

Table 2. WC103 and GaAs compatibility data

Sample #	Base/Semi-conductor Material	Total Heat Treatment Time (hrs)	Original Cylinder Radius(mm)	Reacted Radius (mm)	Reaction Depth mm (%)
NG0	WC103/GaAs	13.31	2.7432	3.2241	0.4809 (70.12)
NG4	WC103/GaAs	18.0	2.7432	3.2931	0.5499 (80.18)
NG5	WC103/GaAs	23.0	2.7432	3.2656	.5224 (76.17)
NG12	WC103/GaAs	28.17	7.7432*	3.1903	0.4471 (65.19)
NG7	WC103/GaAs	34.0	2.7432*	3.3482	0.6050 (88.21)
NG8	WC103/GaAs	40.0	2.7432*	3.3437	0.6005 (87.56)

Note: Original Radius (mm) * - Average of measured values

Table 3. WC103 and CdZnTe compatibility data

Sample #	Base/Semi-conductor Material	Total Heat Treatment Time (hrs)	Original Cylinder Radius(mm)	Reacted Radius (mm)	Reaction Depth (mm)
NT1X	WC103/ CdZnTe	19.0	2.7686	2.8691	0.1005
NT4	WC103/ CdZnTe	30.0	2.7432	2.8667	0.1235
NT5	WC103/ CdZnTe	60.0	2.7432	2.9067	0.1635
NT6	WC103/ CdZnTe	96.67	2.7559	2.9724	0.2165

Table 4. TZM and CdZnTe compatibility data

Sample #	Base/Semi-conductor Material	Total Heat Treatment Time (hrs)	Original Cylinder Radius(mm)	Reacted Radius (mm)	Reaction Depth (mm)
MT1	TZM/ CdZnTe	19.0	2.7432	2.7798	0.0366
*MT4	TZM/ CdZnTe	30.0	2.7432	2.7535	0.0103
*MT5	TZM/ CdZnTe	60.0	2.7559	2.7695	0.0136
*MT6	TZM/ CdZnTe	96.67	2.7432	2.8094	0.0667

* Samples contained no CdZnTe after cutting.

Table 5. Inconel and HgCdTe compatibility data

Sample #	Base/Semi - conductor Material	Total Heat Treatment Time (hrs)	Original Cylinder Radius (mm)	Reacted Radius (mm)	Reaction Depth (mm)
IC1	Inconel/ HgCdTe	10.4	3.2004	3.2487	0.0483
IC2	Inconel/ HgCdTe	12.0	2.9464	3.0150	0.0686
IC3	Inconel/ HgCdTe	13.5	2.9337	3.0302	0.0965
IC4	Inconel/ HgCdTe	15.65	2.9210	3.0328	0.1118
IC5	Inconel/ HgCdTe	20.0	3.048	3.1648	0.1168

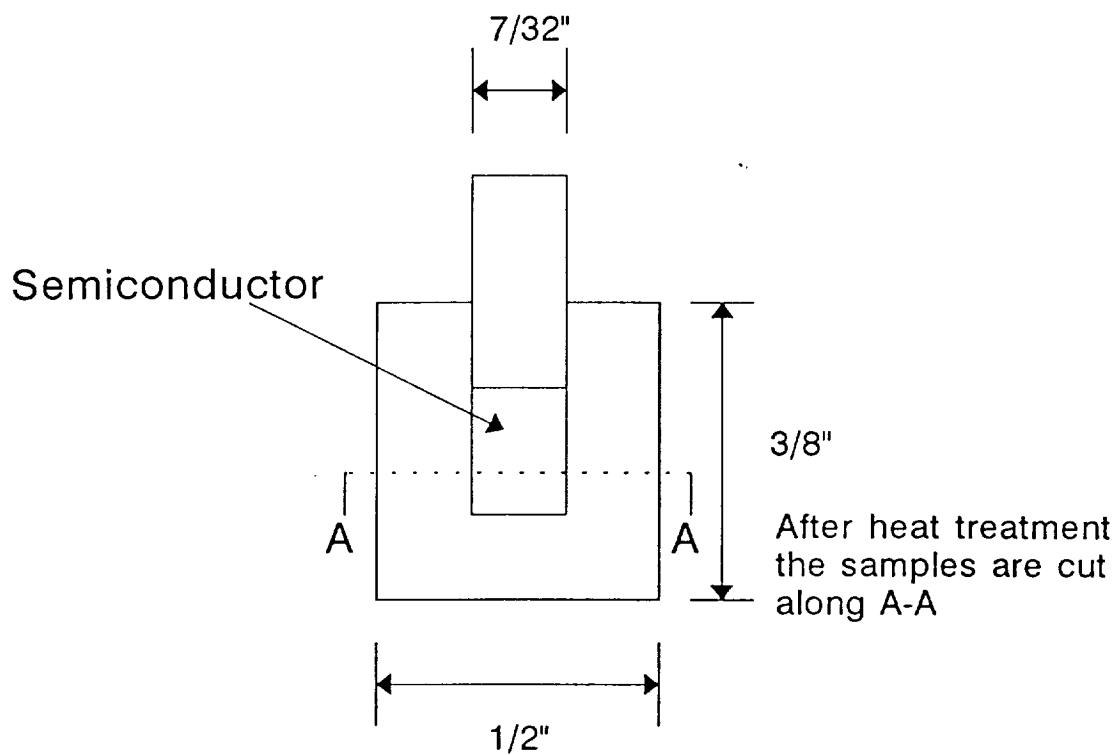


Figure 1. Configuration of sample capsules

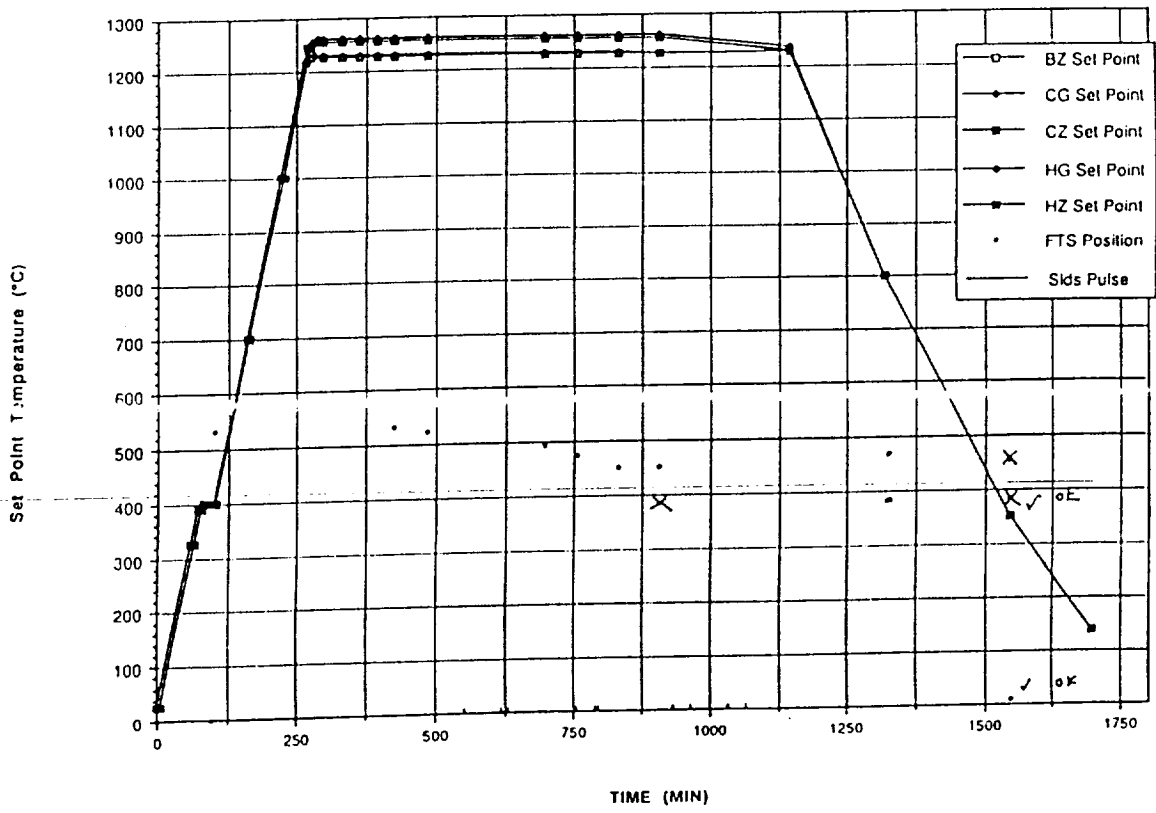


Figure 2. Heat treatments for GaAs

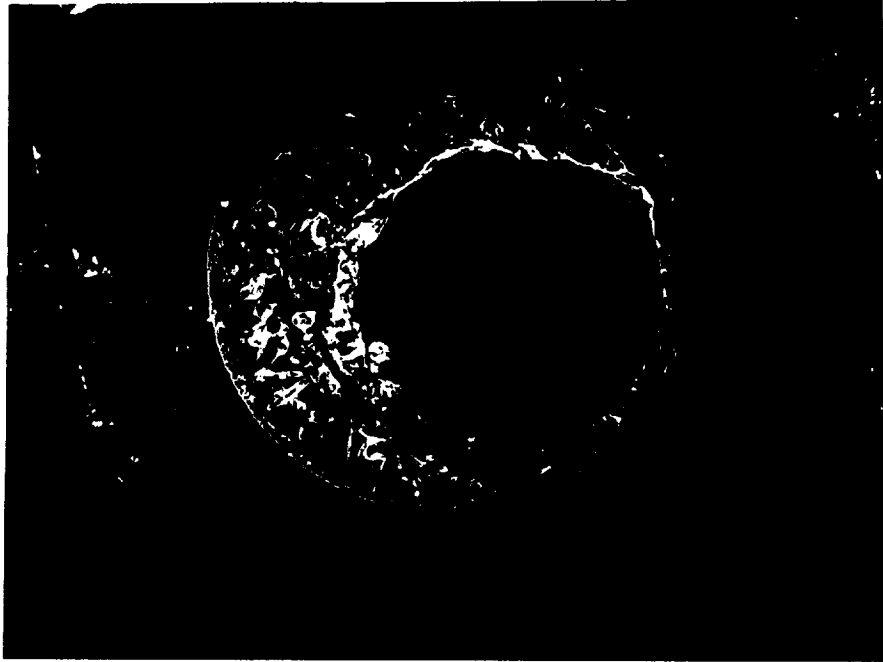


Figure 3. Typical appearance of TZM/GaAs cross section



Figure 4. TZM/GaAs reaction zone

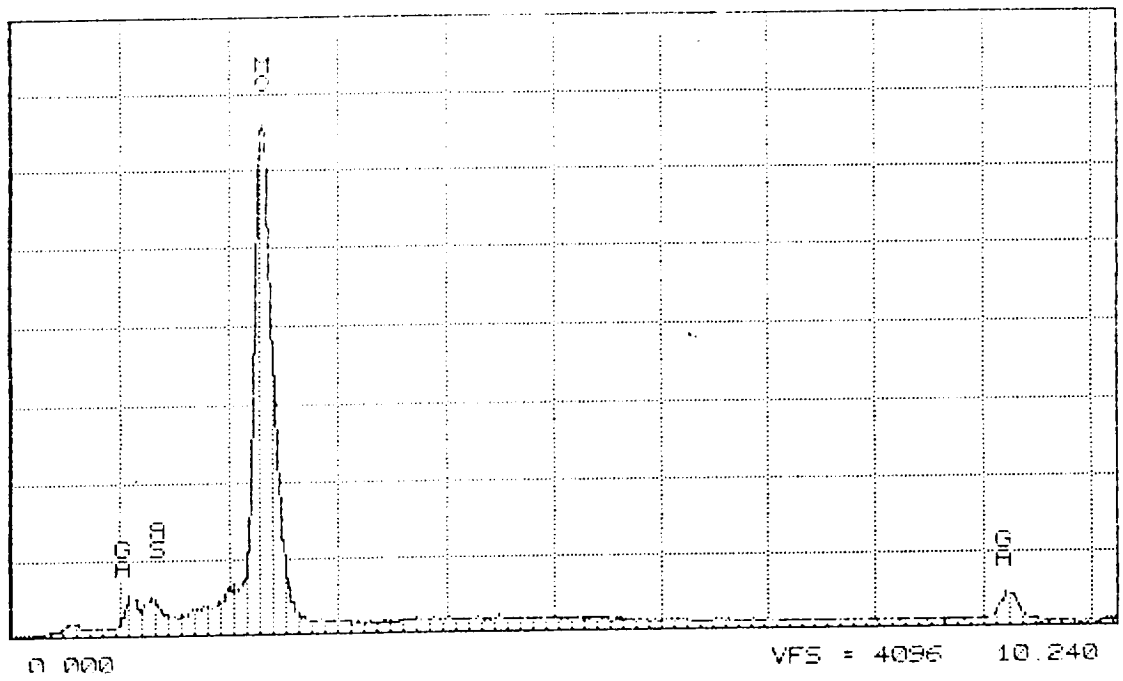


Figure 5. EDS scan at point #1 in TZM/GaAs reaction zone

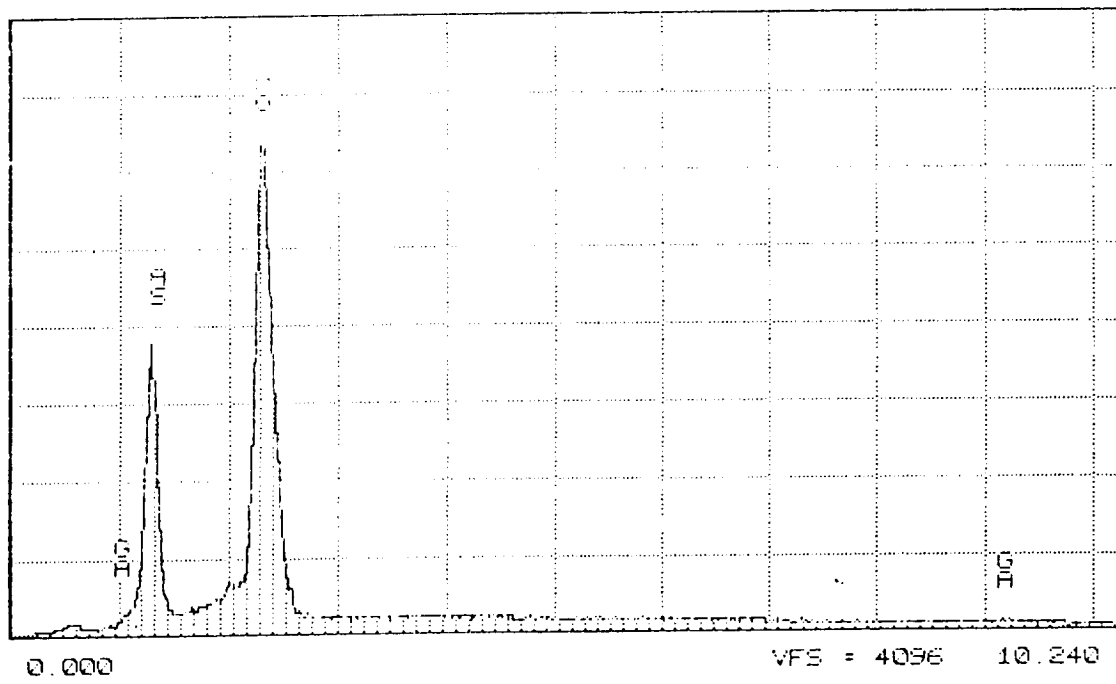


Figure 6. EDS spectrum at point #2 in TZM/GaAs reaction zone

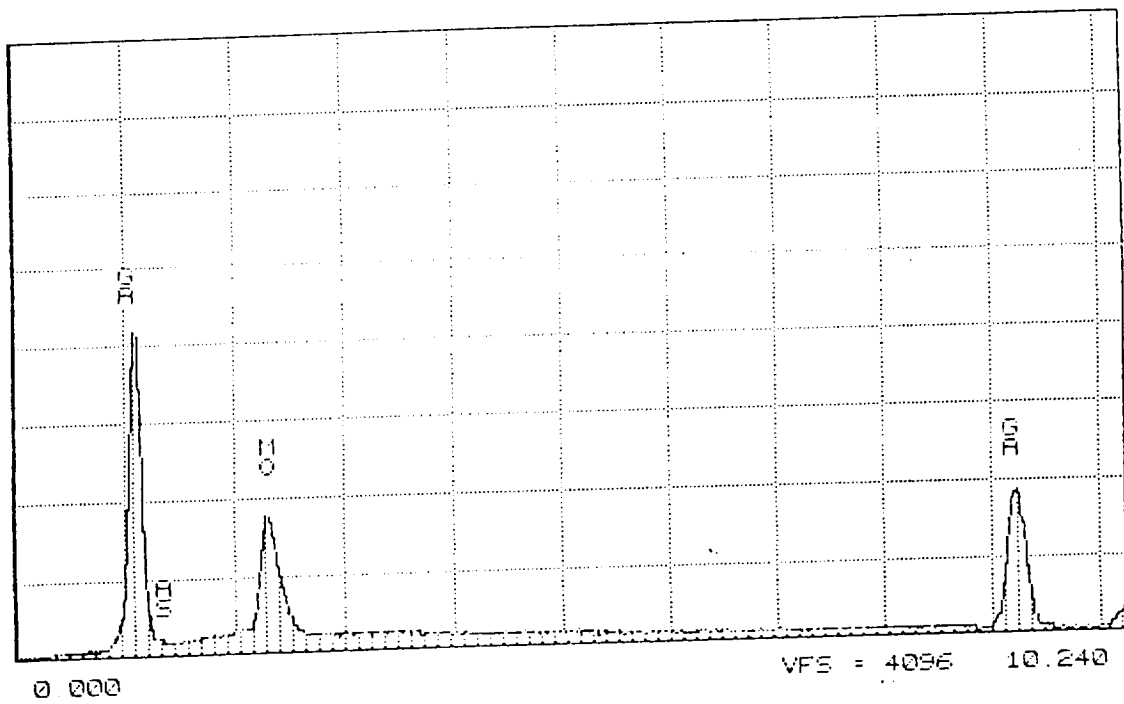


Figure 7. EDS spectrum at point #3 in TZM/GaAs reaction zone

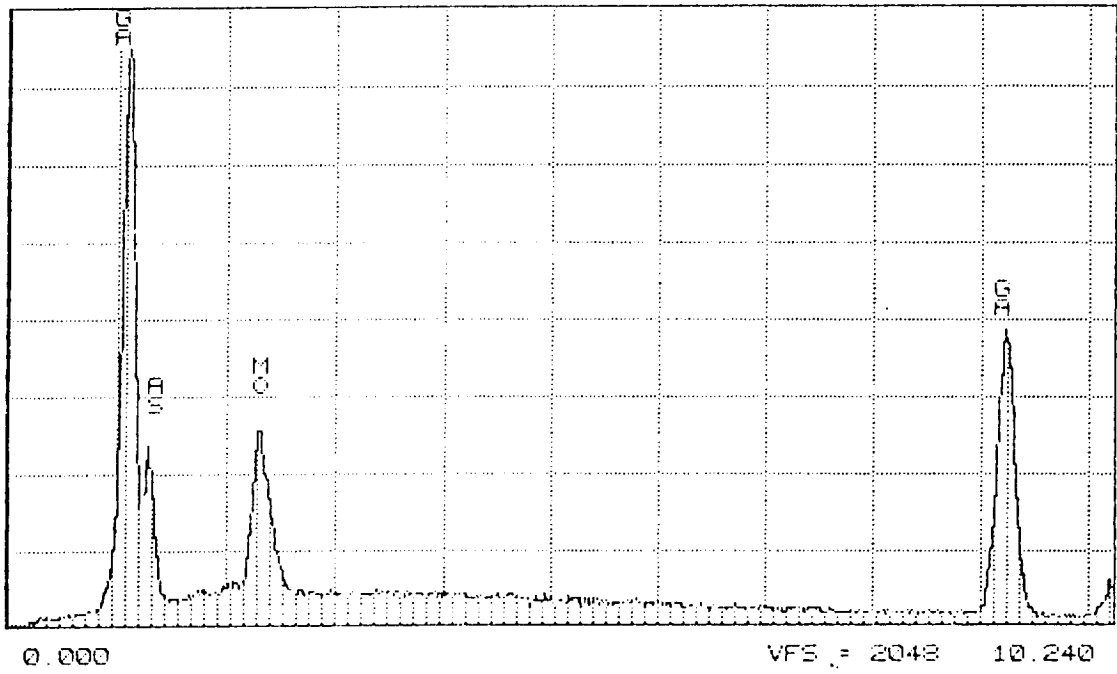


Figure 8. EDS spectrum at point #4 in TZM/GaAs reaction zone

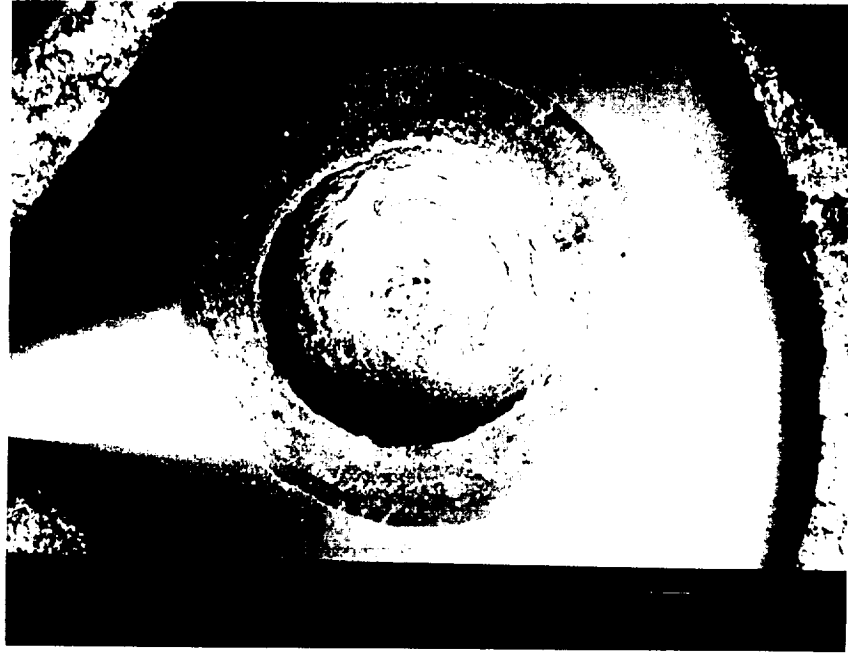


Figure 9. WC103/GaAs sample cross section



Figure 10. WC103/GaAs reaction zone

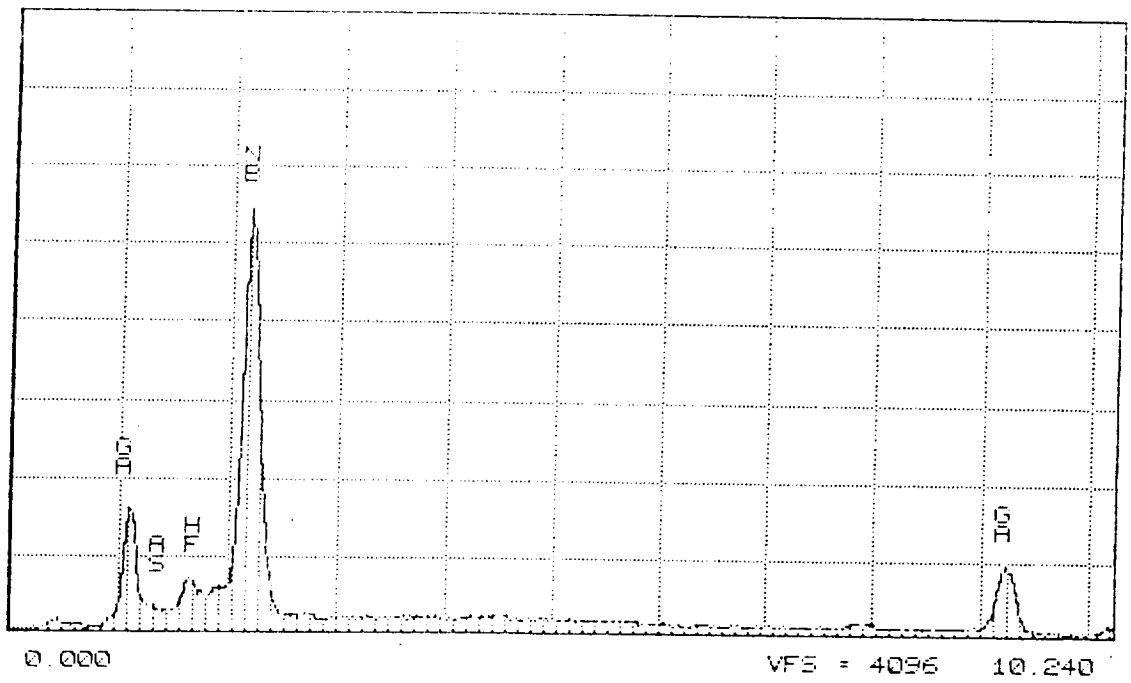


Figure 11. EDS spectrum at point 1 in WC103/GaAs reaction zone

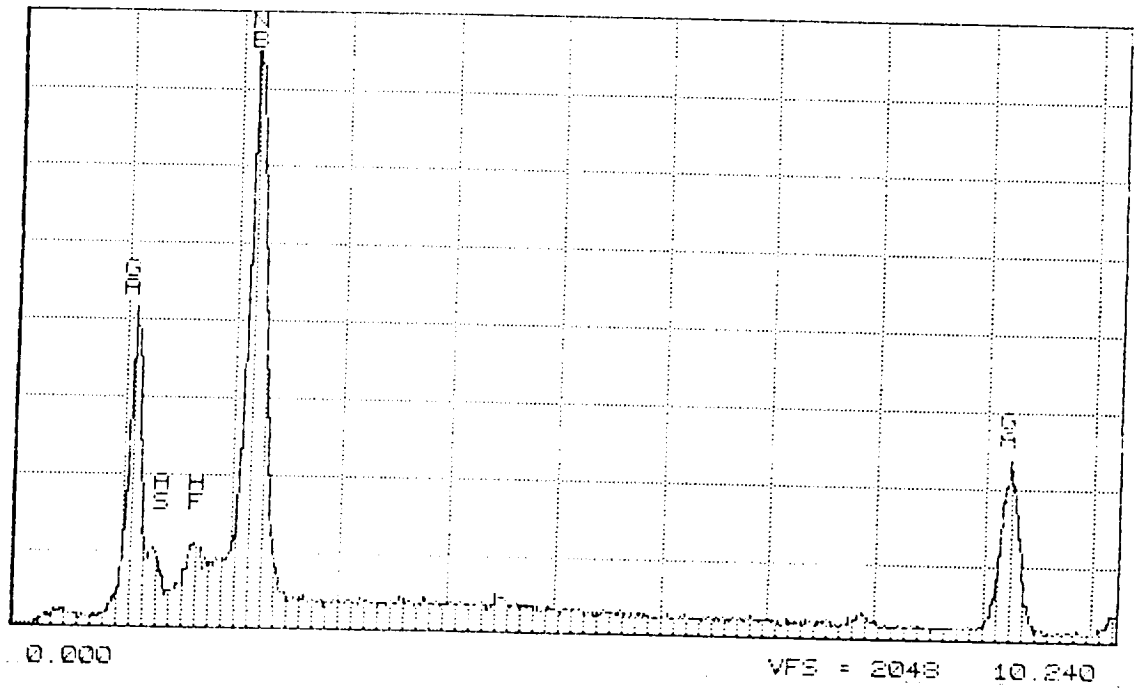


Figure 12. EDS spectrum at point 2 in WC103/GaAs reaction zone

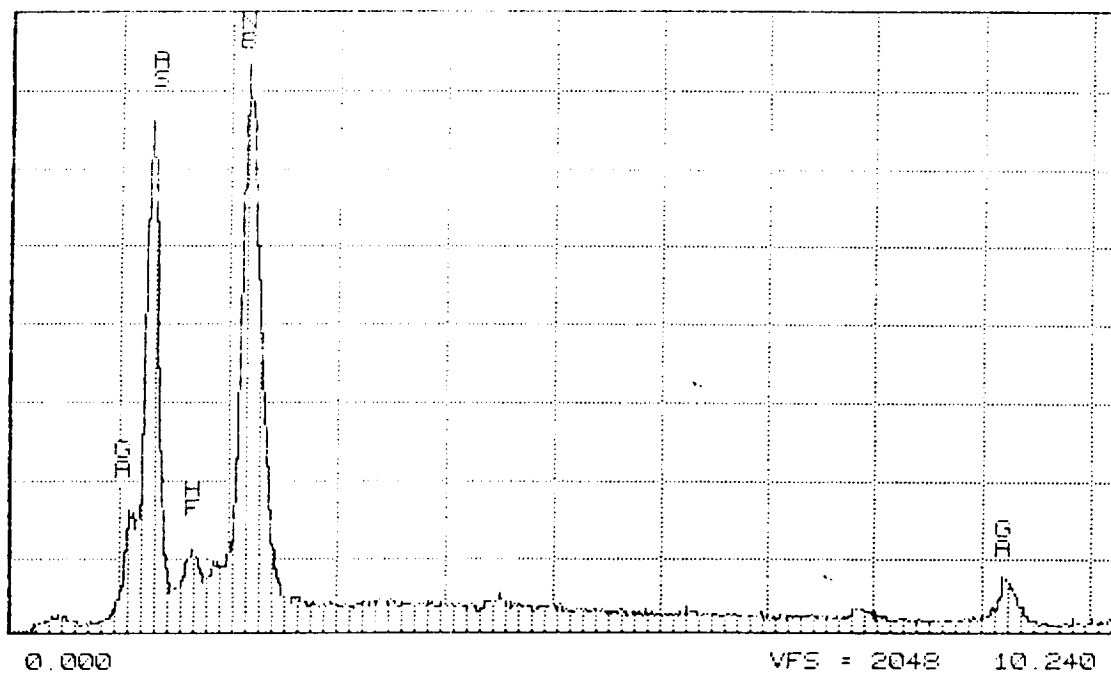


Figure 13. EDS spectrum at point 3 in WC103/GaAs reaction zone

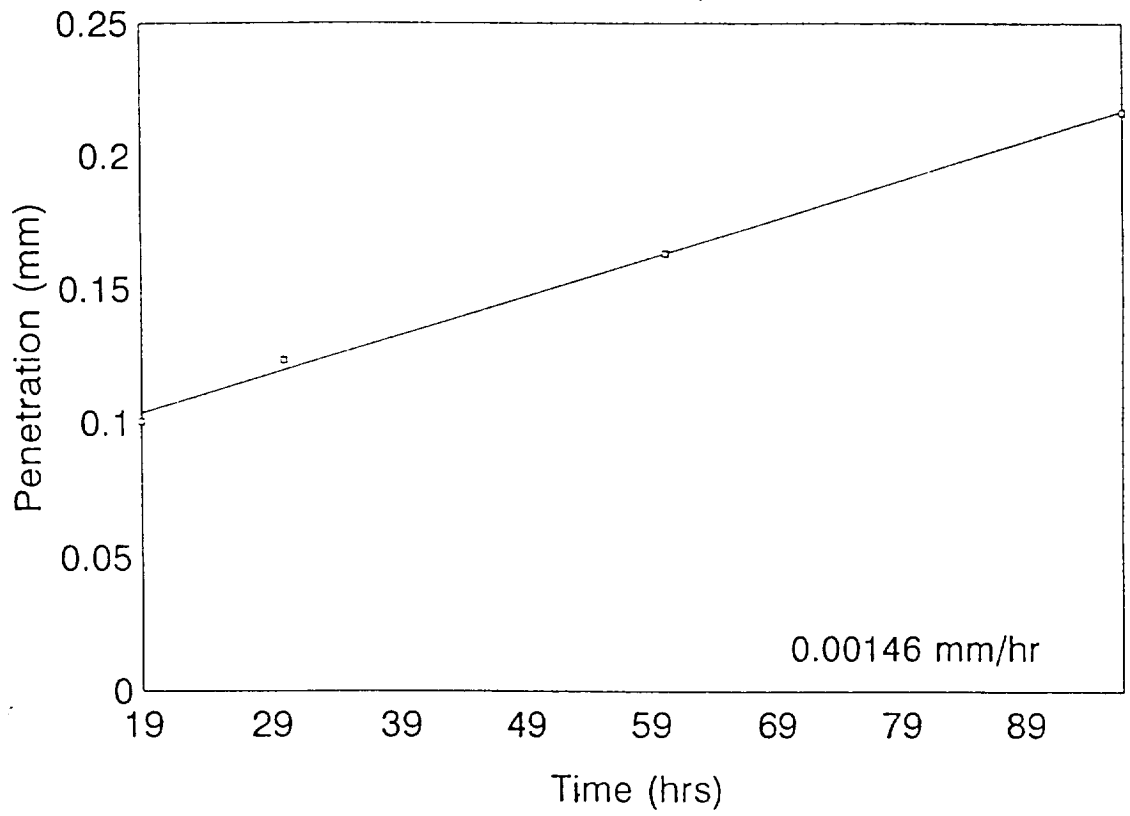


Figure 14. Plot of Wc103/CdZnTe data



Figure 15. WC103/CdZnTe sample cross section

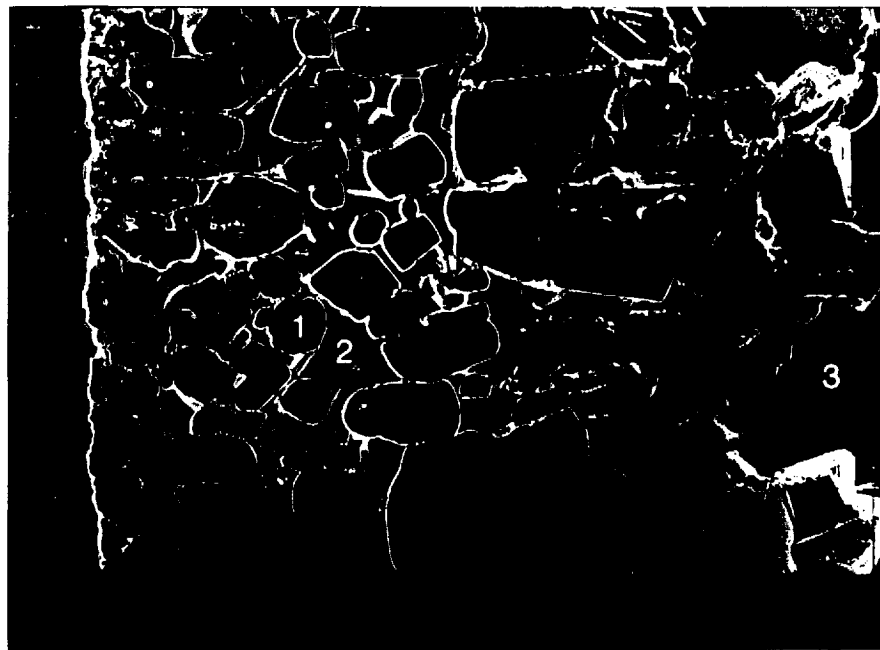


Figure 16. WC103/CdZnTe reaction zone

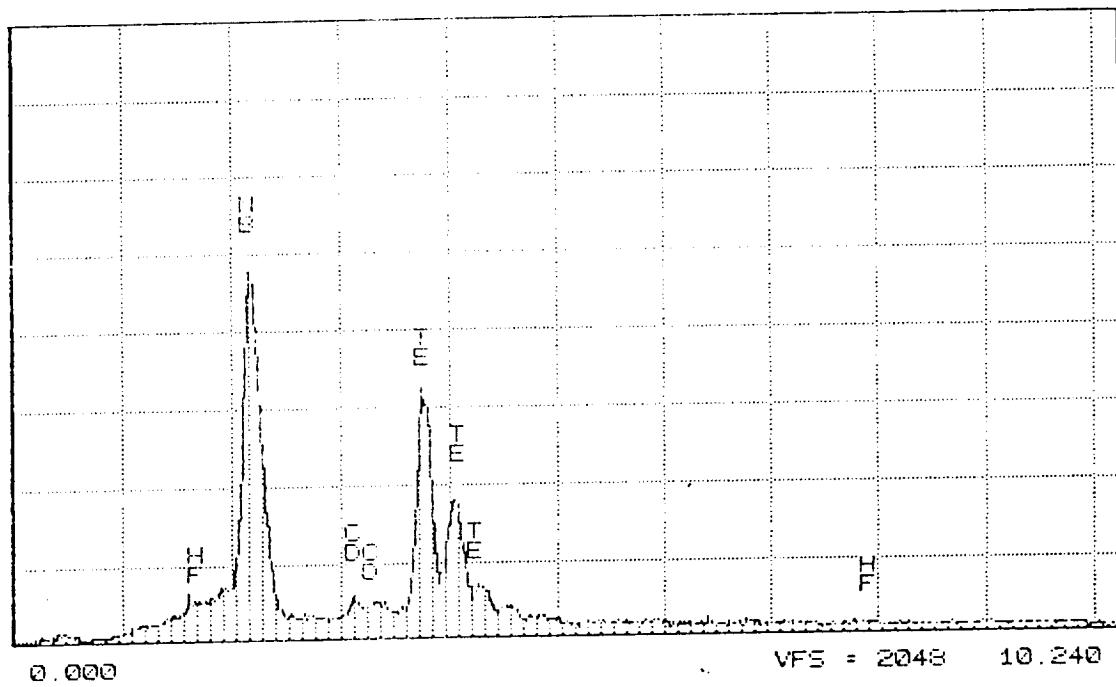


Figure 17. EDS spectrum at point 1 in WC103/CdZnTe reaction zone

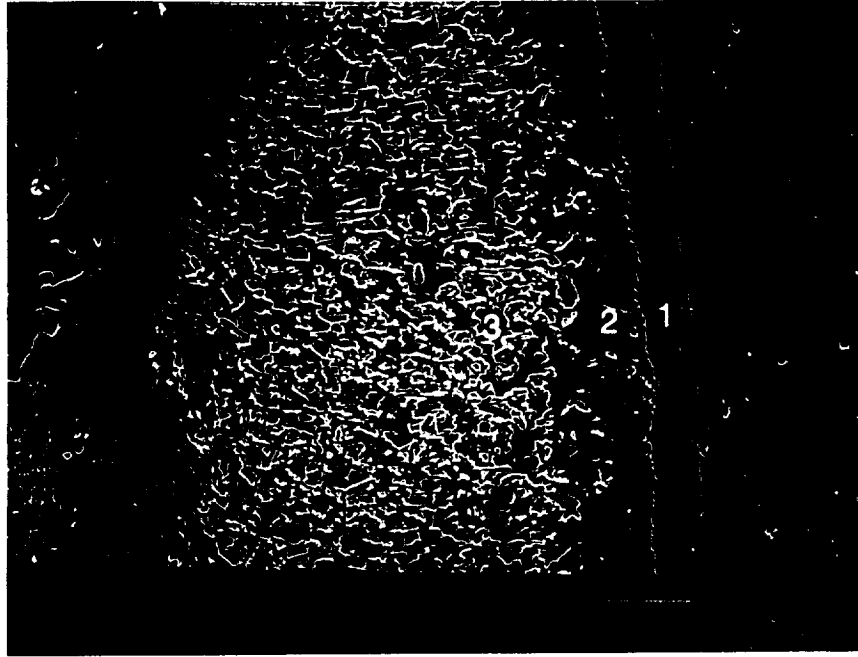


Figure 19. Inconel/HgCdTe Reaction zone

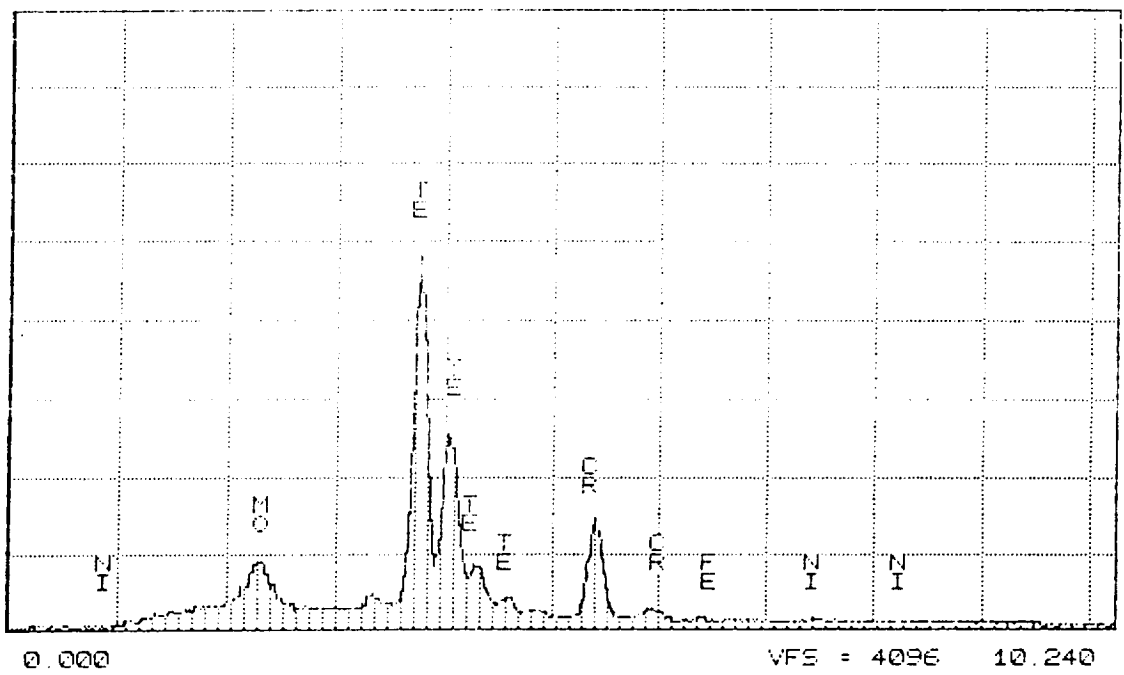


Figure 20. EDS spectrum at point 1 in Inconel/HgCdTe reaction zone

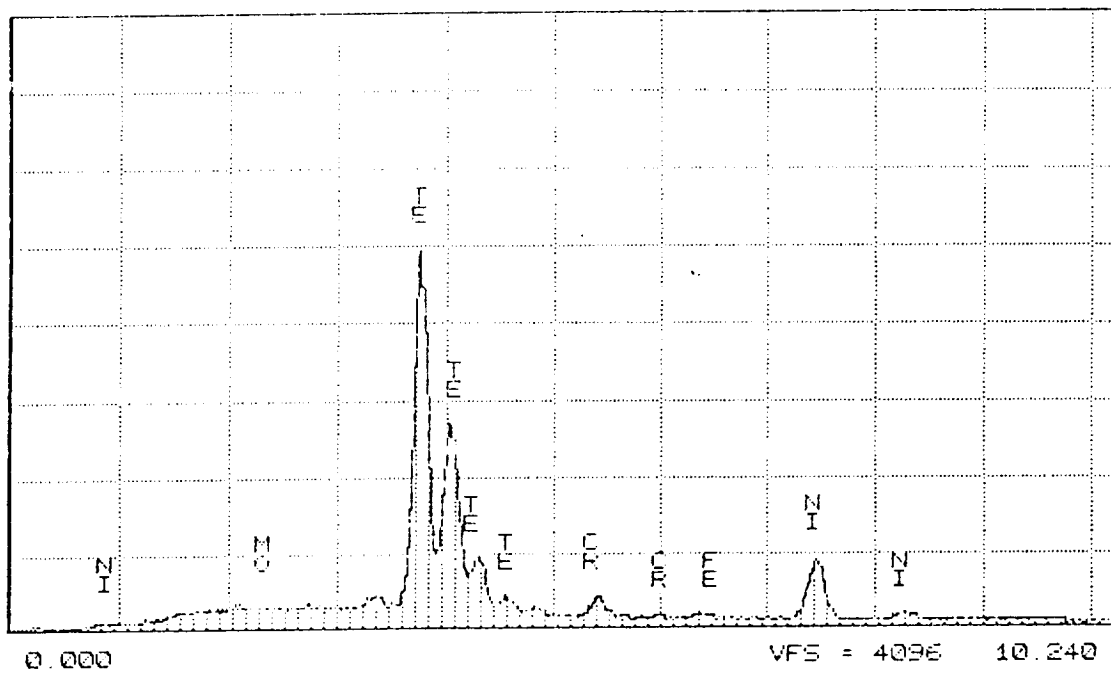


Figure 21. EDS spectrum at point 2 in Inconel/HgCdTe reaction zone

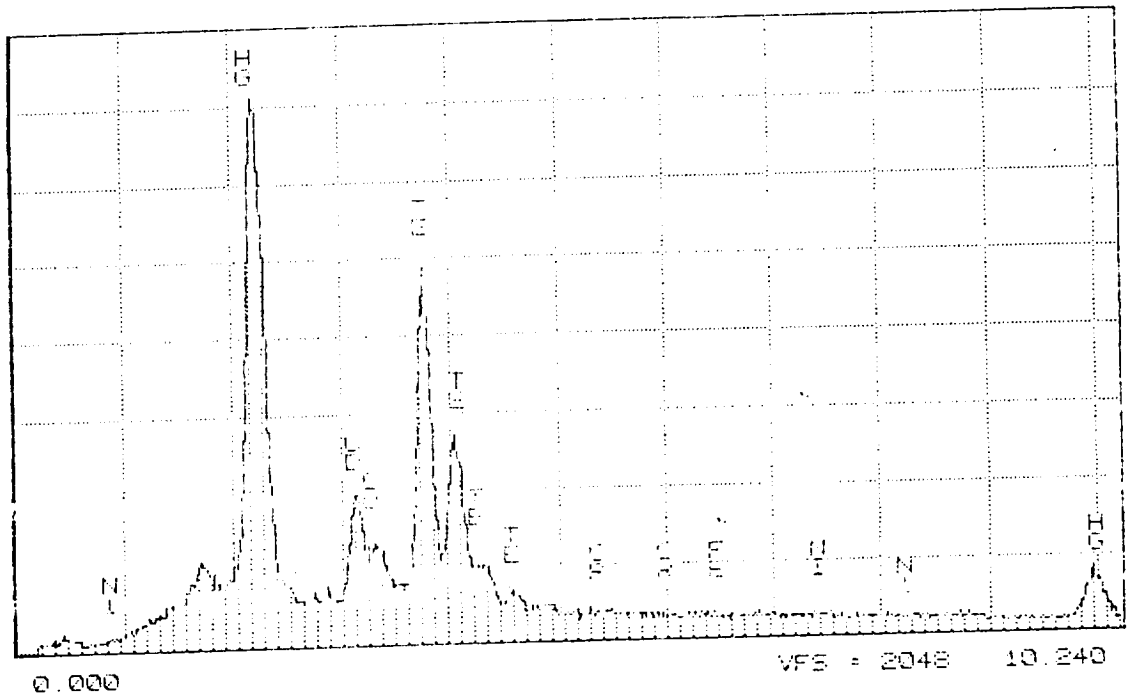


Figure 22. EDS spectrum at point 3 in Inconel/HgCdTe reaction zone