FOR MOUNTED PICTURE PAGES SEE INDEX COPY.

ENGINEERING RESEARCH INSTITUTE
THE UNIVERSITY OF MICHIGAN
ANN ARBOR

DETERMINATION OF CERIUM DISTRIBUTION IN DUCTILE CAST IRON BY AUTORADIOGRAPHIC TECHNIQUE

W. A. Spindler
R. A. Flinn

Project 1862

THE INTERNATIONAL NICKEL COMPANY, INC.
NEW YORK, NEW YORK

March 1957

SUMMARY

When magnesium or cerium is added to cast iron, under proper conditions the graphite crystallizes in spheroidal shape instead of in the usual flake form. To understand the mechanism of this effect, it would be helpful to know the distribution of the element causing spheroidization in the metal structure. Since very small amounts (of the order of 0.02%) are involved, the use of an autoradiographic tracer technique seemed to be indicated.

Radioactive cerium was added to small gray iron melts and specimens were solidified at two different rates. After conventional metallographic polishing, a photographic film was affixed to the polished surface. Following a period of exposure from the specimen, the film was developed in place on the specimen. Since the film was transparent where no radiation occurred, the affected portions of the film could be accurately related to the underlying microstructure.

The observations indicate that cerium is distributed in two ways:

1. A moderate, uniform distribution throughout the metal was obtained in all cases.

2. A higher concentration was also observed interdendritically in the rapidly solidified (white iron) specimen, and in the slowly cooled specimen, in areas of the metal which contained quasi-flake graphite.

Contrary to the work of Hillert and Lindblom on a nickel-carbon alloy, there was no concentration of cerium in the graphite spheroids. Previous findings may have been due to corrosion effects on the film at the spheroids. Spurious effects were encountered in the present work unless special protection was used.

The formation of spheroidal graphite is therefore probably caused by a general effect of cerium throughout the melt such as deoxidation, desulphurization, or surface tension changes, rather than by specific nucleation.

REVIEW OF THE LITERATURE

Earlier metallographic applications of autoradiography have been summarized by Towe, Gomberg, and Freeman.[1] None of these investigations, including the work of Towe, et al., involved work on cast iron.

Hammond[2] used autoradiographic tracer techniques to determine the distribution of radioactive sulphur in spherulitic cast iron. The results were inconclusive because of difficulty with chemical artifacts that occurred in the detecting film.

Hillert and Lindblom[3] used autoradiography to study the distribution of cerium and other rare earth metals in a nickel-carbon alloy in which the graphite occurred in the form of spherulites. These authors concluded that there was a higher concentration of cerium and rare earth metals in the graphite spheroids than in the surrounding matrix of the microstructures. This interpretation of their autoradiographs is open to question since the dark areas over the spheroids could have been chemical artifacts produced by corrosion or by photosensitizing effects. The darkening could also have been due to the low density of the graphite through which more radiation passes to the film than through the surrounding matrix, as pointed out by Michael[4] in his discussion of Hillert's and Lindblom's paper.

Different from other investigators who added radioactive isotopes to their metals, Hillert and Lindblom[3] added non-radioactive misch metal to their nickel-carbon alloy melt. After the usual metallographic preparation, the entire specimen was irradiated in a pile. In the present investigation high-purity cerium metal was irradiated in a pile and then added to the melt of cast iron to produce the spheroidal graphite structure.

Recent investigators have applied the radiation-sensitive layer to the polished metal surface by either the wet process or the stripping-film technique. Wet process autoradiography is discussed by Towe, Gomberg, and Freeman.[1] In this process the detecting layer is formed on the specimen by dipping it in suitable solutions. The stripping-film procedure utilizes a detecting layer that is removed from a supporting celluloid backing and affixed to the polished surface of the specimen to be studied. Because of its simplicity the stripping-film technique was used in this investigation and is described in this report.

PROCEDURE

The procedure is covered under the following headings: The Radioactive Cerium; The Chemical Composition of the Cast Iron; Melting Practice; Heat Treatment; Preparation of Specimens; and Autoradiographic Techniques. A discussion of each of these parts follows.

A. THE RADIOACTIVE CERIUM

The cerium metal used contained 98.6% cerium, 1.0% iron, and other cerium-earth metals. An addition of 0.10 gram of cerium was made to melts in the form

of two small pieces. For the 63-gram melts used in this investigation this constitutes a 0.16% cerium addition. Chemical analyses of the inactive control melt showed that 0.03% cerium was retained in the metal.

The control melt was made using the same procedure as for the radioactive melt except that the cerium metal added was inactive or non-radioactive. This melt was used for chemical analysis since analysis of the active metal was not practicable. Polished specimens of the inactive melt were also carried through the autoradiographic procedures for the purpose of control, to certify that the activity patterns observed were not spurious.

For the radioactive melt the two small pieces of cerium were sealed in a partially evacuated 1/4-inch diameter, 1-1/2-inch long quartz tube to meet the requirements of Oak Ridge National Laboratory. This ampoule was irradiated at Oak Ridge for two weeks at a flux of 1×10^{13} to produce approximately nine millicuries of Ce 141. Seven millicuries of Ce 143 and five millicuries of Pr 143 were also produced.

B. CHEMICAL COMPOSITION OF THE CAST IRON

The composition used for the radioactive melt and the control melt was that which gave the largest volume (about 25%) of spheroidal graphite structure in the central portion of the furnace-solidified part of the melt. The chemical analysis of the control melt was 3.98% total carbon, 2.90% silicon, 0.51% manganese, 0.03 phosphorus, and 0.03% cerium. This composition is approximately the same as that which gave Morrogh and Williams[5] their best microstructures.

C. MELTING PRACTICE

Approximately 63-gram melts were made in the induction equipment shown in Fig. 1. Power was supplied by a mercury-arc converter. The charge consisted of 60 grams of pig iron, 2.7 grams of 50% ferrosilicon, and 0.24 gram of 75% ferromanganese. These materials were broken or cut into pieces small enough to fit inside the smaller alundum thimble in which they were melted.

When the melt attained 2800°F, the power was turned down to allow slow cooling. As the melt reached 2625°F, the cerium addition was made while the power was on to avoid freezing of the small melt by the plungers used for making the additions. The plungers used for making additions were 1/4-inch-outside-diameter quartz tubing that were closed and flattened to a slightly larger diameter on the end. This slight enlargement permitted holding the granular additions on the end of the plunger with thin paper and thread.

Immediately after the cerium addition was made, and with the decreased power still on, half of the melt was sucked up into a 1/4-inch-inside-diameter Vycor tube so that it would solidify rapidly to a white-iron structure. With

the low power still on, the remaining half of the melt in the thimble was inoculated with 0.27 gram of SMZ (silicon, manganese, zirconium) which provided a 0.50% silicon addition. The power was then turned off and this inoculated portion of the melt was allowed to solidify in the furnace to produce a graphitic structure.

D. HEAT TREATMENT

Autoradiographs were made on thin specimens of both the white-iron and graphitic structures as cast. Both materials were also given a ferritizing anneal to observe any change that might occur in the distribution of the cerium. The annealing cycle was 5 hours at 1700°F, cooled to 1300°F in 3.5 hours, and then held at 1300°F for 5 hours.

E. PREPARATION OF SPECIMENS

For autoradiography very thin specimens are desirable to minimize subsurface radiation and thereby improve resolution. The thinnest specimens that could be cut with the equipment available were approximately 0.050 inch thick. This thickness was used for the earlier part of the investigation and these specimens were mounted in bakelite and polished in the usual manner for metallographic examination.

Later, the technique of Plumb[6] was used with some modification to obtain specimens about 0.002 inch thick. At this thickness the metal began to crumble, especially where the structure contained quasi-flake graphite. Plumb's procedure, as modified, consists of removing a polished specimen from its bakelite mounting and cementing it, polished side down, into a recess machined in another bakelite disc. The upper rough exposed portion of the specimen is then carefully removed by hand on emery cloth until the desired thickness is attained.

F. AUTORADIOGRAPHIC TECHNIQUE

Stripping-film autoradiographic procedure was used, utilizing Kodak Autoradiographic Permeable Base Stripping Film "Experimental," 35 mm wide. In this procedure it is first necessary to protect the polished surface of the metal from corrosion by the developing and fixing solutions since the film is processed while remaining on the specimen. Two protecting coatings, one over the other, were applied to the polished specimens. The first coating was deposited by immersing the specimen in a 2.0% solution of Vinylite (Bakelite designation: VYNS) in methyl-ethyl ketone. The second and subsequently applied coating was applied by dipping it in a 2.0% solution of Parlodion (Mallinckrodt Chemical Works) in methanol. The vinylite coating provides the chief protection from corrosion, although the parlodion adds some additional protection. A useful function of the parlodion is that it aids in holding the stripping film to the specimen.

Working in a dark room with a red safelight, a piece of stripping film about the size of the specimen was cut from the roll with a pair of scissors. The emulsion with its gelatin backing was then stripped from the stiff celluloid support, using two pairs of tweezers. In most cases in this investigation the stripped film was placed on the metal specimen so that the gelatin backing separated the emulsion from the upper parlodion coating. This was accomplished by noting that the gelatin backing also separates the emulsion from the stiff celluloid part of the stripping-film roll.

The technique for affixing the emulsion with its gelatin backing onto the metal specimen consists of making a deep pool on the horizontal specimen of water containing 1% of Dupanol "C." This wetting agent aids in getting good contact between the film and the specimen. With a pair of tweezers the piece of stripping was placed on the pool of water and allowed to float for about one minute during which it swelled and enlarged considerably The excess water was now removed with filter paper and the film was adjusted into proper position by tilting the specimen.

The specimen and film were placed in a light-tight box for the desired exposure time at a temperature no higher than 80°F. Excessively high temperatures must also be avoided during applying the protective coatings and during development of the film. The emulsion was developed for ninety seconds at 68°F in a Kodak D-19 solution, using one part of stock solution to two parts of water. Fixing was done in Kodak F-5, or F-6, for two minutes followed by washing for ten minutes. After drying, the film was observed under a microscope while still intact with the specimen to correlate the activity pattern in the film with the microstructure of the specimen. Control specimens of the non-radioactive melt were carried through all operations.

RESULTS

The metal was studied in several conditions—when it was rapidly cooled, solidified in the furnace, and heat-treated. Since the distribution of the cerium in the metal shown by the autoradiographs is related to the cast structure, the various microstructures are considered first, followed by the autoradiographs.

A. MICROSTRUCTURES

That portion of the melt which was sucked up into the 1/4-inch-diameter Vycor tube solidified to a white-iron structure shown in Fig. 3 and, at higher magnification, in Fig. 13. This microstructure is typical of strongly hypereutectic white iron and shows a radial pattern of carbide, and transformed austenite dendrites, extending to the center of the round section. Figure 3

also shows a few graphite spheroids, one of which is shown at higher magnification in Fig. 11 in an unetched specimen.

Heat treatment of this white-iron structure produces small irregularly shaped graphite arranged in radial stringers as seen in Fig. 8, and at higher magnifications in Figs. 16 and 17. The radial pattern of the graphite is similar to that of the carbide and transformed austenite in Fig. 3.

The half of the melt that was allowed to solidify in the furnace had a variable structure shown in Fig. 7. The quasi-flake graphite structure containing a few large graphite spheroids occurred in the outer portions of the casting, whereas the spheroidal-graphite structure occurred in the central region. These two zones of structure, respectively, are shown at higher magnification in Figs. 24 and 19. The matrices of the microstructures of both of these zones had approximately 20% pearlite, but it occurred in larger and more segregated patches in the quasi-flake structures. Flotation of large, irregular, star-shaped graphite occurred in the upper part of the casting.

The ferritizing anneal produced no change in the various types of graphite present in the furnace-cooled casting, but did eliminate the pearlite. The white-iron structure was completely graphitized by this heat treatment to the structure shown in Figs. 16 and 17.

B. AUTORADIOGRAPHS

Since the cerium metal added to the melt had quite high activity, the exposure times were short for autoradiographs made soon after melting. Required exposure times, however, increased fairly rapidly as time elapsed after melting, owing to the relatively short half-lives of the radioactive isotopes present. On the other hand, as the elapsed time after melting increased, the activity of cerium 141 became more and more dominant because of its longer half-life of 32.5 days. The half-life of cerium 143 is 33 hours and it decays to praseodymium 143 which has a half-life of 13.8 days.

Because the autoradiographs in this investigation were made over a period of months, during which time the activity of the cerium decreased markedly, a statement of exposure time in hours has little meaning along. Consequently in this report, exposures are referred to simply as relatively long or short, and for those readers who desire more complete information the exposure for each autoradiograph is detailed in Table I. The specific activities of Ce 141, Pr 143, and Ce 143 during each exposure are given in Fig. 2, as is also their sum which constitutes the total activity.

In this investigation a series of autoradiographs was made at low magnification, mainly 75X, to show the general location and magnitude of the cerium segregation in the several structures. Higher magnification, 500X and 2000X, were then used to investigate the details of these areas of segregation as well

TABLE I

EXPOSURE DATA FOR AUTORADIOGRAPHS

Autoradiograph, Fig. No.	Time, hr	Time Out of Reactor, days	Total Activity, mc/0.1 gm cerium
4	17.5	95	2.3
5	17.5	95	2.3
6	17.5	95	2.3
7	16.3	92	2.5
8	27.0	114	1.5
9	19.0	99	2.1
10	1.0	18	16.6
12	2.5	52	6.6
15	29.0	161	0.6
18	29.0	161	0.6
20	18.0	140	0.9
23	18.0	140	0.9

as to observe the uniform activity pattern throughout the remainder of the structures including the graphite spheroids.

Before discussing specific autoradiographs it is desirable to explain the characteristic features of these pictures in a general way. As radiation emitted by the metal specimen passes through the film, some of the silver grains in the emulsion are affected and appear in the film after development as dark spots under the microscope. A cluster of these spots can be plainly seen in the center of Fig. 20 at a magnification of 500X. The larger number of these spots in the center of this autoradiograph indicates a segregation of cerium in the underlying metal at this location.

Since the emulsion is separated slightly from the metal by the protective coatings and by the gelatin backing of the film it is possible to focus separately on the spots in the emulsion or on the metal surface as desired. The autoradiograph of Fig. 20 is focused on the silver spots, whereas Fig. 21 of the same area is focused on the underlying metal through the film and transparent protective layers. Since this metal specimen has been annealed, the structure consists entirely of ferrite and graphite, and the grain boundaries of the ferrite can be seen in Fig. 21. The general haziness of this photomicrograph is due to the fact that it was taken through the film but the details of the microstructure are well defined.

Figure 10, also at 500X, focused on the silver spots, shows uniformly distributed activity in the underlying metal. Approximately this same amount of uniform activity was shown by all the high-magnification autoradiographs

which indicated that part of the cerium present in the metal was uniformly distributed throughout the structure. Figure 10 also shows that the concentration of cerium in the graphite spheroids is no higher than in the surrounding matrix. Figure 11, taken through the film, shows the radial structure of the graphite spheroids.

1. Autoradiographs at low magnifications.—Comparable autoradiographs were made at 75X on each of the following five unetched structural conditions of the cast iron: white iron, both as cast and after annealing; quasi-flake graphite structure, both before and after annealing; and the spheroidal graphite portion of the furnace-cooled metal, as cast. These autoradiographs were made with relatively long exposures to develop pronounced activity patterns in the emulsion that could be photographed at 75X. Although all these exposures were not made simultaneously, the exposure time multiplied by the specific activity in each specimen was held constant so that the autoradiographs are comparable. The exposure data for each autoradiograph are given in Table I.

Figure 4 shows the radial interdendritic pattern of cerium segregation outward from the center of the cross-section of the 1/4-inch-round white-iron specimen, unetched. This activity pattern follows the radial carbide and transformed austenite-dendrite pattern of the microstructure shown in Fig. 3. In addition to the radial streaks of activity in Fig. 4, a few graphite spheroids are seen which also appear in Fig. 3.

The pronounced segregation of cerium in the outer quasi-flake portion of the furnace-cooled part of the melt is shown in Fig. 5. Figure 6 is the comparison autoradiograph of the central spheroidal-graphite portion of the same casting. The transition from one to the other of these two zones of structures is shown in Fig. 7 at lower magnification. Although there is some segregation of cerium in the spheroidal-graphite structure, it is seen to be much less pronounced than in the quasi-flake part of the casting. Annealing produced no evident change in the degree of cerium segregation present in the as-cast structures, as can be seen by comparing the autoradiographs of Figs. 8 and 4, and Figs. 9 and 5, respectively.

2. Autoradiographs at high magnifications.—The autoradiograph of Fig. 12 is of a typical area of the concentrated activity shown in Fig. 4 of the white-iron structure, taken with less exposure to improve resolution at the higher magnification of 500X. The detecting film was then removed and the photomicrograph of the same area is shown in Fig. 13. The finely dispersed material in Fig. 13 that is present in the active area is shown at higher magnification in Fig. 14. This finely divided material which may possibly contain the segregated cerium has not as yet been identified.

Figure 15 is the autoradiograph, made with less exposure and higher magnification, of a typical area of the segregation in Fig. 8 of the annealed white-iron structure. Figure 16 is the photomicrograph of the same area taken through the detecting film. The most highly active part of an area similar to

Figs. 15 and 16 is shown at higher magnification in Fig. 17 after the detecting film was removed. An unidentified extremely finely dispersed material is present in that part of the structure seen to be most active in Fig. 15.

Figure 18 is the autoradiograph, made with less exposure and higher magnification, of a typical area of concentrated activity in Fig. 6 in the spheroidal graphite structure of the furnace-solidifed part of the melt. The photomicrograph of the same area as in Fig. 18 is shown in Fig. 19 after the detecting film was removed. Although the activity pattern in Fig. 18 is obscured by the pearlite, it is seen that the areas of concentrated activity occur in the pearlite. This circumstance makes it very difficult to identify the active material, if any, in the structure.

Since it appears that annealing causes no diffusion of the segregated cerium, a specimen of the furnace-solidified part of the melt was given the ferritizing anneal to eliminate the pearlite for further study of the segregation in the spheroidal structure. Figure 20 is an autoradiograph of this annealed structure and Fig. 21 is the micrograph of the same area taken through the detecting film. The film was then removed from the metal specimen and a micrograph, Fig 22, at 2000X was taken of the same area where concentreated activity was present.

Figures 23, 24, and 25 were obtained in the same way from a typical area of concentrated activity in the quasi-flake portion of the annealed, furnace-cooled part of the melt. Figure 23 is the autoradiograph; Fig. 24 is the micrograph taken through the film; and Fig. 25 is the micrograph at higher magnification after the film was removed. It is seen that Figs. 13, 14, 17, 21, 22, 24, and 25 all show small particles of an unidentified dispersed material in the areas where concentrated activity occurs.

Furthermore, it is apparent in Fig. 10 and in the areas remaining around the concentrations of activity in all other high-magnification autoradiographs, that there is a moderate, uniform activity throughout all the microstructures in addition to the concentrations of activity. This indicates that part of the cerium in the metal was uniformly distributed in the structure and part was segregated to a varying extent in the several microstructures. Also as seen in Fig. 10, and evident in other autoradiographs, there is no segregation of cerium in the graphite spheroids.

Autoradiographs of non-active control specimens were made throughout this investigation. Decreasing the thickness of the metal specimen from 0.050 to 0.002 inch did not change the uniformly distributed activity pattern noticeably nor did it improve resolution at the segregations. In future work, however, the thinnest possible speciemsn should be used to avoid subsurface radiation effects as much as possible.

REFERENCES

1. G. C. Towe, H. J. Gomberg, and J. W. Freeman, "High-Resolution Autoradiography," National Advisory Committee for Aeronautics Technical Note 3209, July, 1954.

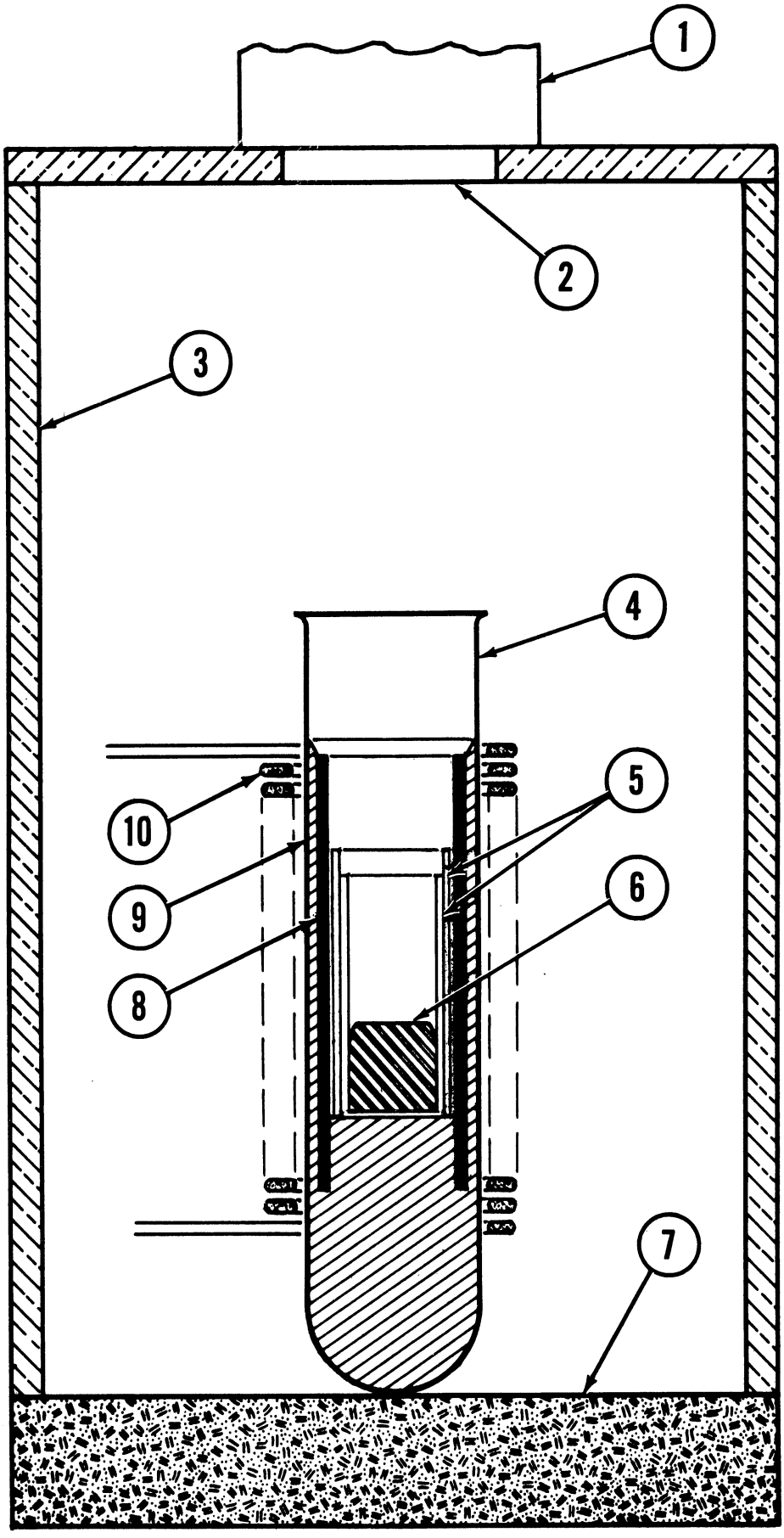
2. H. J. Gomberg, M. J. Sinnott, et al., "High-Resolution Autoradiography for Study of Grain Boundaries in Metals," Final Report of The University of Michigan Engineering Research Institute Project 2029 for U.S. Army Ordnance Corps, February, 1954.

3. M. Hillert and Y. Lindblom, "The Growth of Nodular Graphite," J. Iron and Steel Inst., 176, 5, April, 1954, pp. 388-390.

4. J. Iron and Steel Inst., 178, 2, October, 1954, p. 160.

5. H. Morrogh and W. J. Williams, "The Production of Nodular Graphite Structures in Cast Iron," J. Iron and Steel Inst., 158, 3, March, 1948, pp. 306-322.

6. R. C. Plumb, "Technique of Microautoradiography for Metal Specimens," The Review of Scientific Instruments, 26, 6, May, 1955, pp. 489-493.



Legend

1. Pipe to exhaust fan
2. Opening for operation
3. Transite hood
4. Pyrex test-tube
5. Alundum thimbles
6. Metal being melted
7. Alberene stone
8. Porcelain sleeve
9. Fiberfrax insulation
10. Induction coil

Scale 1/2" = 1 inch

Fig. 1. Induction melting equipment.

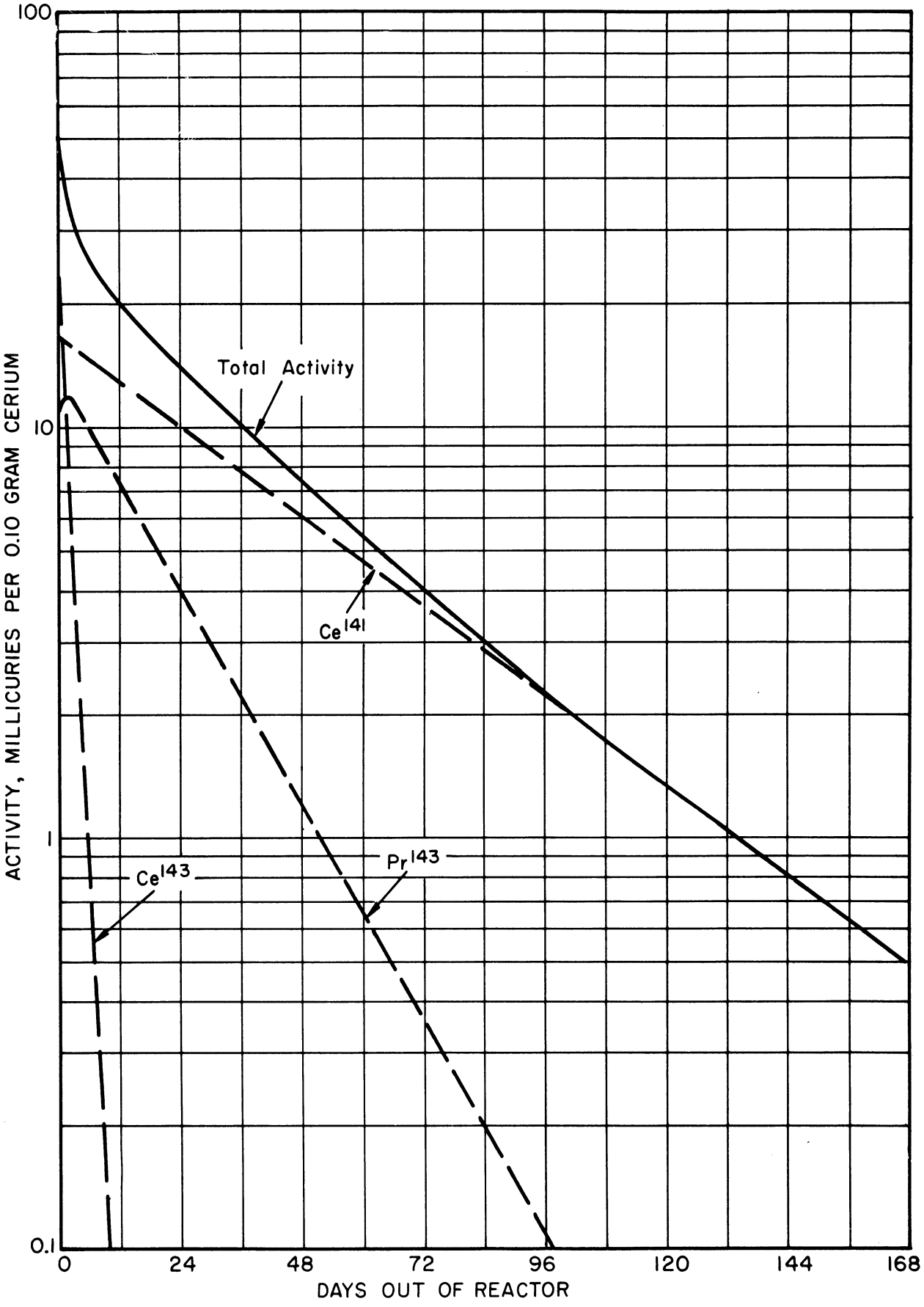


Fig. 2. Activity of 0.10 gram cerium metal versus time out of reactor; irradiation time 14 days at flux density of 1×10^{13}.