

SSC-119

**A REPLICATION TECHNIQUE
FOR THE STUDY OF BRITTLE FRACTURE OF
SHIP PLATE STEEL BY ELECTRON MICROSCOPY**

by
E. C. Haas

SHIP STRUCTURE COMMITTEE

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ADDRESS CORRESPONDENCE TO:

SECRETARY
SHIP STRUCTURE COMMITTEE
U. S. COAST GUARD HEADQUARTERS
WASHINGTON 25, D. C.

January 11, 1960

Dear Sir:

The Ship Structure Committee sponsored an electron-microscopy study at the New York Naval Shipyard to determine if a method could be developed to correlate the microstructure of ship plate steel to its brittle fracture transition temperature. Herewith is the Final Report, SSC-119, A Replication Technique for the Study of Brittle Fracture of Ship Plate Steel by Electron Microscopy by E. C. Haas.

This project has been conducted under the advisory guidance of the Committee on Ship Steel of the National Academy of Sciences-National Research Council.

This report is being distributed to individuals and groups associated with or interested in the work of the Ship Structure Committee. Please submit any comments that you may have to the Secretary, Ship Structure Committee.

Sincerely yours,



E. H. Thiele
Rear Admiral, U. S. Coast Guard
Chairman, Ship Structure Committee

Serial No. SSC-119

Final Report
of
Project SR-123

to the

SHIP STRUCTURE COMMITTEE

on

A REPLICATION TECHNIQUE FOR THE STUDY OF
BRITTLE FRACTURE OF SHIP PLATE STEEL BY ELECTRON MICROSCOPY

by

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Washington, D. C.
National Academy of Sciences-National Research Council
January 11, 1960

ABSTRACT

This investigation was undertaken to study the applicability of electron microscopy in determining the relationship of microstructure of ship plate steel to its brittle fracture transition temperature in order to obtain a broader understanding of the phenomena involved in the brittle failure of plating in ship hulls under service conditions. The results for a series of specimens of differing transition temperatures indicate that there is a relationship between the degree of separation of cementite lamellae and the temperature in the transition from predominantly ductile to predominantly brittle fracture. An increase in cementite ordering is correlated to higher transition temperatures.

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INTRODUCTION

After a discussion of the inadequacy of ordinary test methods and inspections in explaining the brittle failures that have occurred in ships, the Committee on Ship Steel of the National Academy of Sciences-National Research Council decided in 1950 that, in order to obtain a broader understanding of the phenomena involved in brittle failure of plating in ship hulls under service conditions, an investigation should be undertaken to 1) develop electron microscope techniques peculiar to metallurgy, and 2) study the applicability of electron microscopy in determining the relationship of the microstructure of ship plate steel to its brittle fracture transition temperature.

Following formal approval of this recommendation by the Ship Structure Committee, two projects of a joint nature were initiated under the title "Electron and Optical Microscopy," one at Stevens Institute of Technology and the other at the Material Laboratory of the New York Naval Shipyard. The Material Laboratory was to independently perfect preparatory phases of the replication techniques that were suitable for imaging fractured surfaces by means of the electron microscope, collaborate with the investigations at Stevens Institute of Technology, in which the technique was being evaluated with respect to fractured surfaces of ship plate steels, and then attempt to determine through use of the electron microscope if a relationship existed between the microstructure of ship plate steel and its brittle fracture transition temperature.

Inasmuch as various techniques such as the Formvar one-step plastic replica,¹ the two-step carbon replica,² and the all-metal replica³ are now or have been available since this work was undertaken, this report will describe how the replicas for ship plate steel were made. It will also attempt to correlate the microstructure of the ship plate steel and its transition temperature.

The validity of the replication technique used in this study on the fractured surfaces of ship plate steels has been previously reported in the Ship Structure Committee series.⁴

POLYSTYRENE-SILICATION METHOD

The 5-step procedure used to obtain replicas for the electron microscope studies is as follows:

1. Preparation of polystyrene negative-replica. The metal surface to be replicated is coated with a film deposited by a solution containing 1 per cent of polystyrene dissolved in benzol. When the surface is dry, this operation is repeated twice, and then a final coat of 6 per cent polystyrene in benzol solution is applied.
2. Stripping of polystyrene replica. A block of polystyrene, 5 to 10 mm thick and of an area sufficient to cover the replica, is cemented to the polystyrene film with methyl methacrylate monomer and is heated at 65 C for one hour. The specimen and plastic are placed on dry ice for 15 minutes and then pulled apart.
3. Formation of silica positive-replica. The plastic block is placed, replica side up, 7.5 cm below the center of a loop of 24-gage, B&S tungsten wire, which is 15 cm in diameter and located in a vacuum-evaporation unit. The wire is coated with a solution of Ludox, * the assembly is evacuated to a pressure below 10^{-3} mm of mercury, and a current of approximately 20 amperes is passed through the wire until evaporation of the silica is complete.
4. Shadowing of silica replica. The silica-coated plastic replica is placed 10 cm above a small graphite crucible containing 5 to 10 mg of germanium, the shadowing material. The plane of the replica is inclined 30° to the line from its center to the crucible. After evacuation to a pressure below 10^{-3} mm of mercury, the crucible is heated by the cone of 24-gage B&S tungsten wire in which it is supported until an iridescent film of purple hue is formed on the silica surface. The time and temperature for the formation of this colored film must be found by experiment but should be of the order of 15 seconds at 2700 C.
5. Stripping and mounting of silica replica. The silica-coated plastic is im-

*Ludox--Trade name for a colloidal silica solution supplied by E. I. DuPont de Nemours & Co., Inc., Grasselli Chemicals Dept., Wilmington, Delaware.

mersed in a solution containing 85 parts ethyl bromide and 15 parts of benzol until the polystyrene dissolves sufficiently to allow the silica film to float free. A half-inch square of 200-mesh screen, held by a pair of forceps, is used to catch the silica film immediately after it is disengaged from the plastic. The film is washed by successive transfers to fresh ethyl bromide-benzol solutions. After washing, the film is examined under an optical microscope to locate unbroken areas, which are then punched out, along with the supporting screen, for mounting in the specimen holder of the electron microscope.

An example of replication by the above procedure on the fracture surface of a semikilled project steel "C" formed by the Navy Tear Test is shown in Fig. 1. Initially, the specimen replica was examined visually by traversing it under the electron beam and viewing the magnified image on the fluorescent screen of the microscope. After the replica had been scanned and studied sufficiently to reveal the characteristic elements of its structure, micrographs were made of those areas that best represented and illustrated the composite impression received during the scanning process. The specimen was again polished, etched, replicated, and examined. This process was repeated until it was determined that the resulting structure was not produced by imperfections in the replica technique. Figures 2 and 3 contain micrographs of views taken from separate replicas which had been made from newly polished and etched surfaces of a project steel "A" specimen and a project steel "C" specimen, respectively. To be assured, however, that the greater detail revealed by the silica-replica method was not a part of the replica itself, smooth glass slides and mica sheets were replicated by this technique. A complete absence of spurious structure was noted. In this manner, many of the so-called artifacts of replication were eliminated from consideration.

The polystyrene-silica replication technique shows the structure replicated in finer detail than do the conventional one-step plastic replica techniques, such as the Formvar replica method. This can be attributed to the fact that the final silica replica is much thinner than can be obtained by any one-step method; hence the irregularities in its surface as it follows the structure of the material



Fig. 1. An electron photomicrograph of a polystyrene-silica replica, germanium shadowed at 30°, formed from the rough fractured surface of a project steel "C" Navy Tear Test specimen having a ductile break at 150 F. 3200 X 3.5 = 11,200.

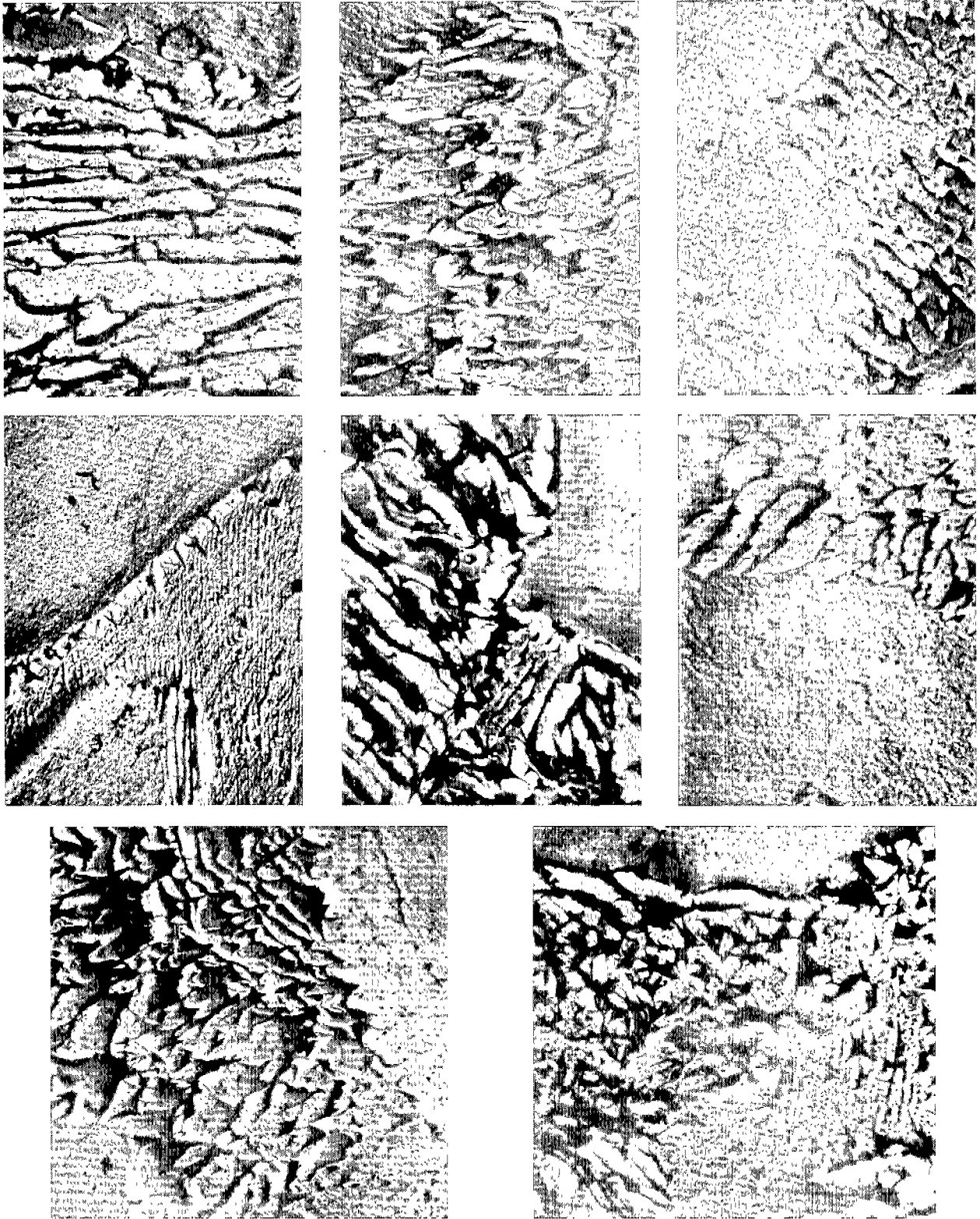


Fig. 2. A verification of the accuracy of the polystyrene-silica replication procedure is illustrated by the variety of structures shown in these electron photomicrographs taken from separate replicas, germanium shadowed at 30°, and different areas of the same mechanically polished, nital etched, project steel "A" specimen. 3200 X 1.25 = 4000.

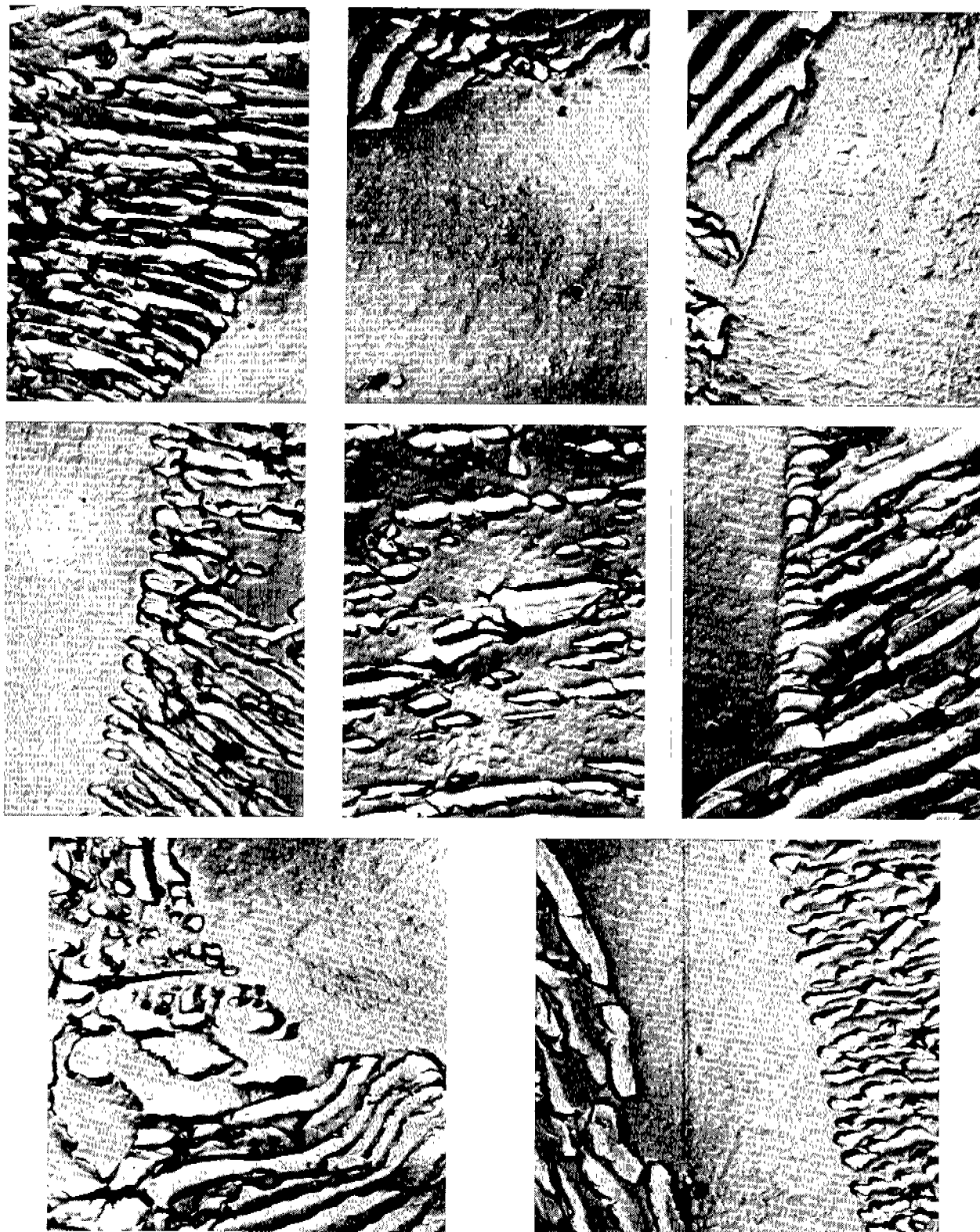


Fig. 3. A verification of the accuracy of the polystyrene-silica replication procedure is illustrated by the variety of structures shown in these electron photomicrographs taken from separate replicas, germanium shadowed at 30°, and different areas of the same mechanically polished, nital etched, project steel "C" specimen. 3200 X 1.25 = 4000.

it replicates constitutes a greater percentage of the total thickness and thus results in correspondingly greater percentage differences in the electron beam transmitted.

On the basis of the foregoing discussion, it was concluded that a technique had been developed which met the testing requirements of the Ship Structure Committee's program.

THE RELATION OF MICROSTRUCTURE TO THE TEAR TEST TRANSITION TEMPERATURE

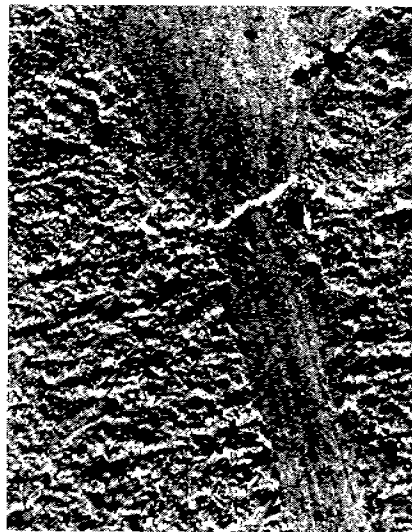
The steel specimens chosen for this phase of the study covered Tear Test transition temperatures ranging from 60 F to 120 F. (The Tear Test transition temperature is here defined as the temperature at which the fracture surface changes from a predominantly ductile to a predominantly brittle appearance.) The chemical composition of the steel is given in Table I. Each specimen was polished, etched, and replicated. From the very large number of areas of each specimen studied and micrographed, micrographs were selected for each transition temperature on the basis that the views could be considered characteristic of the structure examined and that an operator familiar with structure could correctly match micrographs and specimens. Aside from the areas of ferrite, which have been largely excluded, the selection method chosen is believed to illustrate not only the predominant, but also the most distinctive, structure of each specimen.

Selected micrographs of the several specimens of ship plate steel examined are shown in Fig. 4. The significant difference in the structure of these specimens at electron microscope magnifications is in the spacing of the cementite lamellae. The specimens of higher transition temperature show a greater spacing of these lamellae.

An attempt to further correlate transition temperatures to microstructure of the specimens was undertaken based on the heat capacities of the various steels. Wafers of metal, measuring 1/4 in. square by 1/16 in. thick and weighing approximately one gram, were cut from the several samples and adjusted to the same weight by dressing with a file. These wafers were fashioned into thermocouples by spot-welding 30-gage, B&S constantan and iron wires to alternate corners. The



Medium Steel A-1
T.T.T.T. 60 F



Project Steel A
T.T.T.T. 70 F



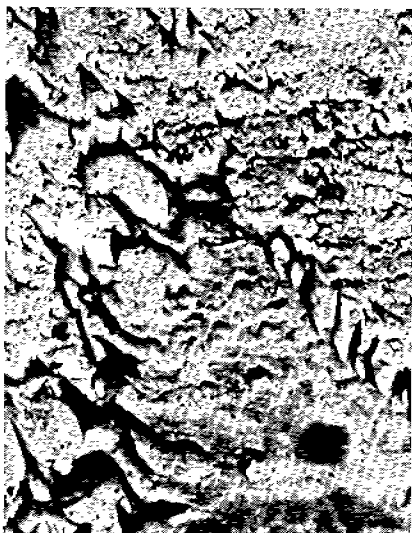
Medium Steel A-4
T.T.T.T. 80 F



Medium Steel A-2
T.T.T.T. 90 F



Medium Steel A-1
T.T.T.T. 60 F



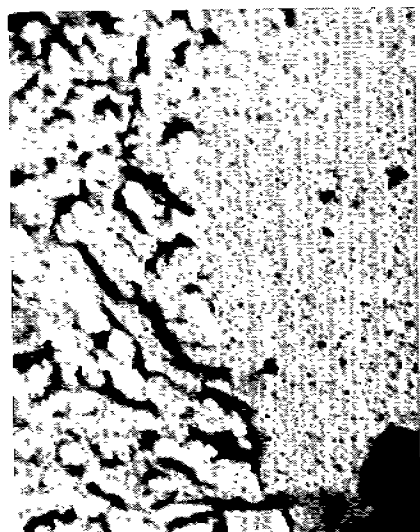
Project Steel A
T.T.T.T. 70 F



Medium Steel A-4
T.T.T.T. 80 F



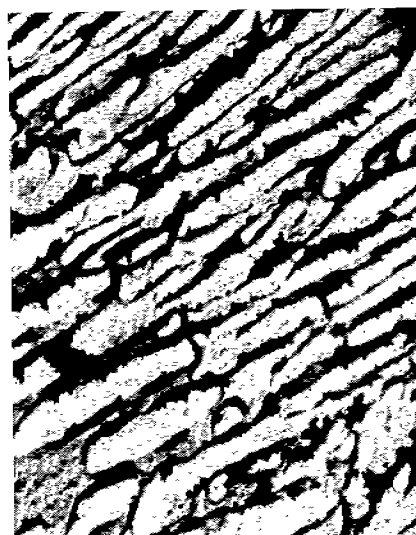
Medium Steel A-2
T.T.T.T. 90 F



Medium Steel
T.T.T.T. 100 F



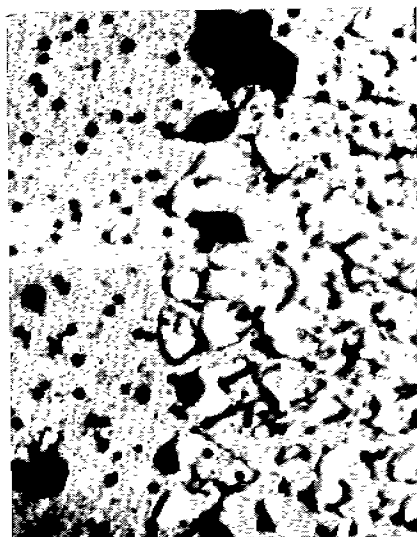
Medium Steel
T.T.T.T. 110 F



Project Steel C
T.T.T.T. 120 F



Medium Steel
T.T.T.T. 100 F



Medium Steel
T.T.T.T. 110 F



Project Steel C
T.T.T.T. 120 F

Fig. 4. A relation between microstructure and Tear Test transition temperature is verified in these electron photomicrographs of polystyrene-silica replicas, germanium shadowed at 30°, of several ship plate steels, each having a different Tear Test transition temperature. The specimens of higher transition temperature show a greater spacing of the cementite lamellae.

5000 X 1.75 = 8750

TABLE 1.
CHEMICAL ANALYSIS (IN PER CENT) OF SAMPLES OF SHIP STEEL

Element	Project A		Project C		A-1	A-2	A-3	A-4
	Mill	U of C	Mill	U of C				
C	0.23	0.26	0.24	0.24	0.22	0.25	0.24	0.24
Mn	0.47	0.50	0.49	0.48	0.47	0.49	0.48	0.49
P	0.011	0.012	0.015	0.012	0.008	0.009	0.010	0.010
S	0.042	0.039	0.033	0.026	0.021	0.028	0.022	0.027
Si	0.02	0.03	0.043	0.05	0.05	0.05	0.04	0.04
Cu		0.03		0.03	0.034	0.032	0.025	0.033
Ni		0.02		0.02	0.02	0.02	0.03	0.02
Cr		0.03		0.03	0.035	0.030	0.026	0.032
Mo		0.006		0.005	0.003	0.003	0.004	0.003
V								
Al		0.012		0.016	-.005	-.005	-.005	-.005
Sn		0.003		0.003	0.036	0.006	0.010	0.006
Ti		---		---	---	---	---	---
N		0.004		0.009	-.005	-.005	-.005	-.005
TTTT* (°F)		70		120	60	90	100	80

*TTTT - Tear Test transition temperature

Notes: Comparative analyses are given for project steels A and C from the laboratories of the supplier (Mill), University of California (U of C), and the New York Naval Shipyard (NYNS).

-.005 indicates less than 0.005%

thermocouples were then heated to 500 F and subsequently plunged into an acetone bath cooled to -80 F with dry ice. As the wafers cooled, the thermocouple output was fed into a Millivac amplifier connected to a Sanborn recorder from which cooling curves, such as those shown in Fig. 5, were obtained.

The heat capacity of a material is defined as the amount of heat required to raise a unit mass of material one degree in temperature. The unit of heat, or energy, is either the British thermal unit or the foot-pound. On this basis, the ordinate of the cooling curves could be converted to energy units in order to place the following discussion on specific terms. However, since the correlation to be made is on a relative basis as an indication of a trend, the cooling curves are used without converting terms.

As may be noted from Fig. 5, each curve contains two abrupt changes in curvature in the 100 to 480 F range. An area under each curve was formed by extending a horizontal line from the lower knee and a vertical line from the upper knee. The area was then measured by counting the blocks of the cross-sectioned paper enclosed by the geometry of the figure; the value for each area is recorded on the figure. These values, if converted as explained previously, can now be considered as the amount of energy that had been stored in each wafer at 500 F.

An arbitrary ratio of the area under each curve to the area of the specimen of lowest transition temperature is given in Fig. 5 to indicate the relative increase in stored energy in specimens of higher transition temperature. Cooling curves of wafers of lead and copper (not shown) gave a smooth temperature drop approximating a logarithmic function of temperature with time and gave no indication of abnormal release of energy in the temperature range selected. Referring back to the steel wafers, the greater release of energy during the cooling of specimens of higher transition temperature may indicate a higher order of crystallinity in these specimens compared with those of lower transition temperature. The better formed and separated cementite areas shown in the electron micrographs of the specimens of higher transition temperature would suggest this higher order of crystallinity.

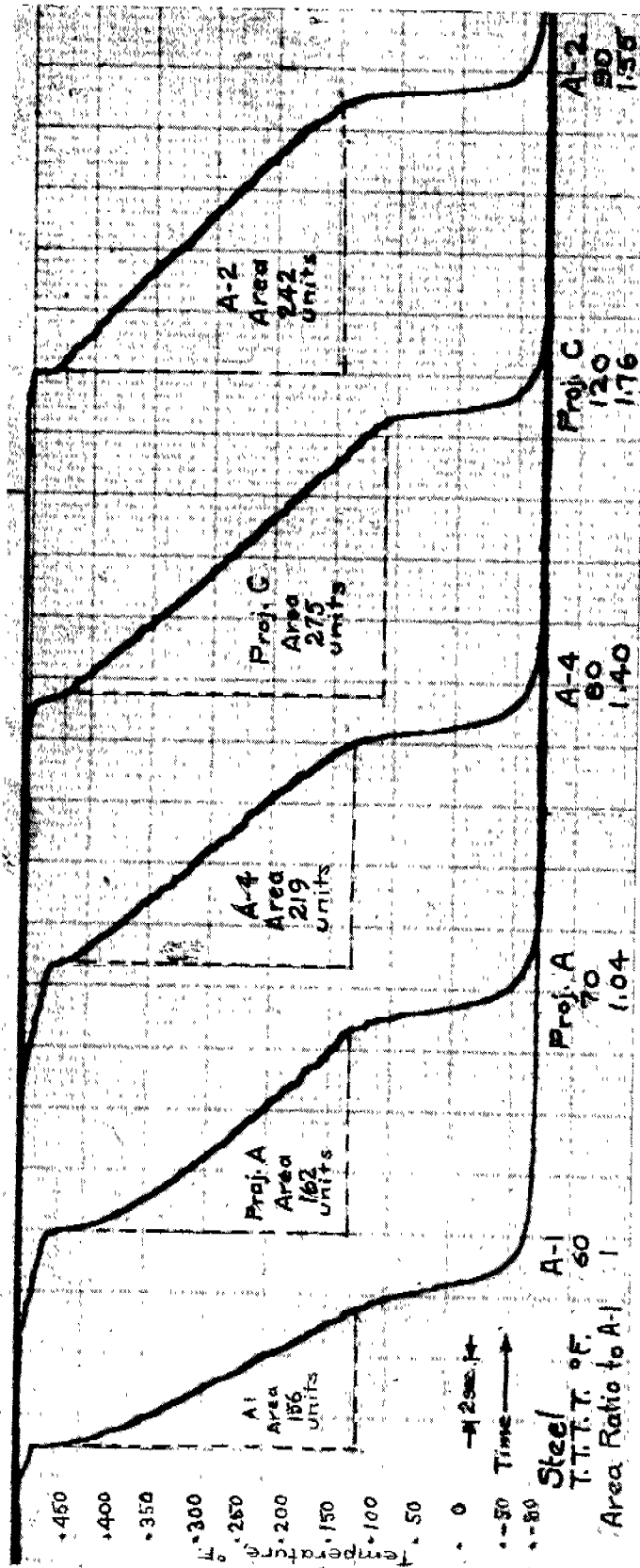


Fig. 5. Cooling curves showing relationship between stored energy and Tear Test transition temperature (T.T.T.) of ship steel in the temperature range of 500 to -80 F.

CONCLUSIONS

It is concluded that information obtained through the use of an electron microscope is potentially useful in extending an understanding of the phenomena involved in brittle fracture of ship plate steel. The work described here has resulted in:

- a. The development of a satisfactory method for imaging both polished and etched surfaces, as well as fracture surfaces of steel specimens at high magnifications.
- b. The postulation of a relationship between cementite ordering and the temperatures in the transition range from predominantly ductile to predominantly brittle fracture of ship plate steel.

ACKNOWLEDGMENT

The work described in this report was performed in the Electron Microscopy Unit of the Physical Chemistry Section under the supervision of A. Gaines, Jr., Unit Head. The replication technique was developed by A. Reisman. A. Reisman, B. L. Gilbert, M. Berkenblit, and F. Nesh successively employed this technique in producing the electron micrographs described and made other important contributions to the results reported. The Wrought Metals and Radiography Section of the Metallurgy Branch provided the specimens and the Tear Test transition temperature values.

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