INTERPRETING GRAPHITIZATION

A Report for Power Plant Engineers

By
Helmut Thielsch, Metallurgical Engineer
Industrial Piping Division

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GRINNELL COMPANY
INC.
FOUNDED 1850
260 West Exchange Street
PROVIDENCE 1, RHODE ISLAND

The power industry has been vitally concerned with graphitization ever since the brittle failure in a welded carbon-moly steel pipe in the main steam line at the Springdale Station of the West Penn Power Company in January 1943.

Because severe graphitization reduces considerably the ductility and toughness of the affected areas, periodic examination of valve and pipe joints in high-temperature piping is essential to prevent costly failures and contingent danger to life and property. For example, a recent routine examination of a main steam line of a power plant revealted a 1 in. deep crack around the circumference of a 1 3/4 in. thick valve-to-pipe joint. This crack, illustrated in Fig. 1, is in the heat-affected zone of the valve, parallel to and approximately 3/32 in. away from the weld metal. Examination under the microscope established that this cracking occurred in a severely graphitized zone which is shown in Fig. 2. Further embrittlement and propagation of the crack might have resulted in a very serious failure in the main steam line. This valve has been replaced to remove this hazardous condition.

MATERIALS

Graphitization is associated primarily with carbon steels in long-time service above 800° F and carbon-molybdenum steels above 900° F. Rolled, forged or cast materials prepared by a high-aluminum deoxidation practice (over 1 1/2 lb. Al per ton of steel) usually are considered highly susceptible to graphitization. The low-aluminum deoxidized grades (less than 1/2 lb. Al per ton of steel) are considered fairly resistant to serious graphitization - although they are not always completely immune. In fact, a recent investigation of a coarse grained, silicon-killed steel used in a petroleum refinery installation showed heavy graphitization. In a steam power system serious graphitization in a silicon-killed steel so far has been found only in one installation. Thus, it is advisable to examine periodically silicon-killed steel piping.

1/2 Cr - 1/2 Mo materials so far have shown resistance to graphitization in service up to at least 950° F. Similarly, the 1 Cr - 1/2 Mo and 1 1/4 Cr - 1/2 Mo grades appear to be resistant up to about 1050° F, although at these temperature levels very limited service data are available to date.

Rolled and forged carbon, carbon-moly and 1/2 Cr - 1/2 Mo steels, from which pipe for steam power systems is fabricated, are now made by the steel mill with a deoxidation practice which limits the maximum permissible aluminum addition to 1/2 lb. Al per ton of steel.

Cast steels, as used in valve bodies of carbon and carbon-moly steels, generally are made by a melting practice with 2 lbs. or more aluminum per ton of steel. The main reason for this is that under ordinary foundry conditions this amount of aluminum is necessary to prevent gas formation in the molds. Although a few foundries have been able to limit the aluminum addition to 1/2 lb. Al per ton of steel, the resulting castings may be considerably more expensive. Since the addition of 1 1/4% chromium and 1/2% molybdenum is likely to inhibit serious graphitization, it is usually economical to specify chrome-moly alloy valve materials.

Since castings, as a general rule, are likely to contain more carbon and aluminum than the corresponding grades of wrought or forged piping materials, the periodic inspection of carbon and carbon-moly valve materials is particularly important.

METALLURGICAL CONSIDERATIONS

Graphite is free carbon which has little strength, very low ductility and very low resistance to mechanical or thermal fatigue or shock. The physical metallurgist considers its formation as a nucleation and growth process which takes place on long-time exposure at temperatures above 800° F. Graphitization is the result of the diffusion and coalescence of atomic carbon in solution in the steel matrix and the decomposition and diffusion of iron carbide (cementite) into ferrite and free carbon and the subsequent diffusion and coalescence of the latter.

When the graphite occurs in form of nodules distributed at random throughout the steel matrix, its effect upon the mechanical properties of the steel is rather insignificant. However, where the graphite segregates in clusters of nodules along zones or forms continuous chains, the mechanical properties in the affected area may be considerably or even seriously reduced.

A narrow band of particularly unstable carbide and ferrite supersaturated with carbon tends to occur at the extremity of the heat-affected zone in the region where the temperatures resulting from the welding operation reach approximately 1325° to 1425° F for a very short time. Subsequent prolonged service above 800° F may cause particularly severe graphitization in this zone - usually about 1/16 to 1/8 in. from the weld.

The degree of graphitization depends primarily upon the composition and thermal history of the steel. For the same type of steel, an increase in the carbon content would tend to increase the amount of graphite that may form.

Alloying or residual elements, which tend to form carbide particles, inhibit graphitization. Thus, chromium, molybdenum, manganese and vanadium are beneficial. If present in a sufficiently large quantity, these elements may prevent graphitization. However, some of these elements may be undesirable because of their effects upon the welding characteristics of the steel.

SAMPLING

Because of the severe consequences of failures in steam power systems, many power companies have in the past checked, and are periodically checking, the condition of welded joints in pipe and valve materials susceptible to graphitization.

The method most widely used consists of removing boat-shaped slices from welded joints by means of the so-called "weld-prober," illustrated in Fig. 3. The slice is taken across the weld and should include at least 1/2 to 1 in. of base metal at each side of the weld. Typical examples are illustrated in Fig. 4. When properly prepared, the weld-probe slice provides sufficient material for a metallographic examination and one bend test, Fig. 5. Pipe or valve sections of such dimensions as to make attachment of the weld-prober impossible may require special sectioning procedures, as trepanning or drilling (see Fig. 1).

Upon removal of the slice from the pipe, the cavity is filled by arç welding, Fig. 6. This is followed by a stress relieving operation. Where rehabilitation of the piping system is contemplated, the stress relieving heat treatment may be omitted or deferred until the weld probe specimen has been examined. For example, if graphitization is found to be sufficiently severe to necessitate immediate rehabilitation of the affected joints, the final stress relieving operation would place the joint into the proper condition, as required by the various Codes.

For economic reasons, only one specimen is ordinarily removed from the weld joint. However, since the amount and type of graphitization may vary around the circumference of the pipe joint, the removal of two or three specimens is advisable - particularly where moderate to severe graphitization is suspected. In particular, in cast valve steels where deoxidation was made in the runner box, the aluminum distribution tends to be non-uniform. The resulting differences in the stability of the metallurgical structure may cause a considerable variation in the "degree" of graphitization.

Although it may often be sufficient to examine only one end of a pipe, differences in the stress, welding and post-heating conditions may have resulted in different "degrees" of graphitization at each pipe end, so that sampling of both ends is advisable. On cast valve steels, it is particularly desirable to examine both ends because of the greater possible variation in the composition of the material.

GRADING GRAPHITIZATION

Since the degree of severity, (i.e. the level of safety of each joint in a steam power system), depends upon the form, shape and distribution of the graphite particles, a relative classification is not readily accomplished. Also, there is no sharp delineation between "severe" and "moderate" graphitization.

The photomicrographs and bend tests obtained from a weld-probe specimen leave room for considerable latitude of interpretation. Careful analysis of such additional operational factors as temperature and pressure cycling, thermal or mechanical fatigue and shock, external loading, section thickness, etc., is also necessary. When of significant magnitude, these factors may contribute to a reduced level of safety of mild or moderately graphitized piping.

On the basis of the 10 years of research in the laboratories of the Grinnell Company, a grading system of graphitized zones has been established which is illustrated in Fig. 7.

The microstructures shown in Fig. 7 generally correspond to the following bend angles (test strips bent to the point where a 1/16 in. long crack is first observed in the heat-affected zone):

Graphite observed in microstructure	Bend angle
mild	over 90°
moderate	45-90°
heavy	30-45°
severe	15-30°
extremely severe (dangerous)	below 15°

Obviously, the "degree" of graphitization may fall between these gradings.

REHABILITATION

Where significant quantities of graphite have been found in the heat-affected zone in piping or valve materials to warrant concern, several procedures may be employed to restore the steam power system to a safer operating condition. These are:

(1) Solution heat treatment.

(2) Removal of graphitized area in the heat-affected zone by (a) partial or (b) complete grooving out and rewelding.

(3) Replacement of graphitized pipe or valve sections.

The choice of the proper procedure depends primarily upon the degree of graphitization, the estimated future life and operating conditions of the particular power system and certain economic factors. Sometimes moderately or even heavily graphitized pipe or valve joints which do not show cracking are temporarily rehabilitated by the solution heat treatment until the next shutdown of the steam power system, or until replacement pipe or valve sections can be obtained. It is important to realize that both the solution heat treatment and the rewelding procedure serve only as temporary cures.

The continuous use of materials susceptible to graphitization should be accompanied by periodic examination of weld-probe specimens to study the progress of graphitization. The results of such periodic studies also assist in the selection of a suitable rehabilitation procedure.

Solution Heat Treatment

The solution heat treatment consists of heating the graphitized area to above the upper critical (transformation) temperature of the steel. At these temperatures the "ferritic" steel has transformed into an "austenitic" steel in which the graphite will dissolve. Upon subsequent cooling, the carbon will again be in "solution" or will form cementite particles. A commercial solution heat treatment consists of heating for two to four hours at temperatures between 1700 and 1750° F, depending upon the type of steel and the degree of graphitization. This is followed by controlled cooling to 1000° F at a rate of 300° to 400° F per hr.

The major advantage of this procedure is that it is less costly than rewelding or the replacement of pipe or valve sections. However, where long operating periods of five, ten or even more years are involved, the solution heat treatment provides, at best, only a temporary cure. It is generally accepted that graphite will re-form more rapidly and in less time in the solution heat-treated, heat-affected zone than it did in the original stress relieved weld. It is also believed that the solution of graphite during the solution heat treatment leaves small voids in the steel matrix. These voids continue to act as local stress raisers so that the solution heat treatment does not improve materially the ductility and toughness over that of the previously graphitized area. Thus, subsequent regraphitization during service is likely to further weaken the material.

One large utility company, having first solution heat treated one steam power system, decided subsequently to cut out all welds and heat-affected areas and reweld the entire system. Rewelding in the first place would have been considerably less costly.

Rewelding of Graphitized Area

In this procedure the graphitized area is first removed by flame or arc grooving and/or grinding and is rewelded subsequently. A stress relieving heat treatment should follow the welding operation.

In the case of moderate graphitization, partial removal of the graphitized area may be adequate. The groove is cut to about 1/16 in. from the backing ring on the inside diameter of the pipe or valve. Where graphitization has occurred only on one side of the weld, as may be the case in the valve side of pipe-to-valve joints, the procedure illustrated in Fig. 8 should be followed. Where graphitization has occurred on both sides of the weld, the recommended procedure is illustrated in Fig. 9. The new groove is approximately 1/3 to 1/2 wider than the original groove.

The advantage of this procedure is that fit-up, groove protection and back-up are not required. Of course, proper supporting of the piping is essential in order to prevent cracking in the weld area and not disturb the cold spring (prestress) in the pipe line at room temperature. It must be realized that a small zone of graphitized steel remains at the root of the new weld deposit.

Where the degree of graphitization has been sufficiently heavy to reduce seriously the ductility and toughness in the graphitized area causing cracking to occur in bend specimens at an angle of less than 45°, it may be advisable to remove completely the heat-affected and weld areas. The cut ends should then be pulled together, fitted-up and rewelded as illustrated in Fig. 10. In rigid systems it may be desirable to build up the groove faces with weld metal and grind to obtain a standard edge preparation prior to the final welding operation of the two ends.

Where necessary, suitable pipe sections should be inserted, preferably of 1/2 Cr - 1/2 Mo, 1 Cr - 1/2 Mo or 1 1/4 Cr - 1/2 Mo steel to replace one or several removed sections, as illustrated in Fig. 11. Generally, the 1 1/4 Cr - 1/2 Mo grades are most readily available.

In due time graphitization may reoccur in the new heat-affected zones adjacent to the weld. Depending upon the materials involved and the postheating cycle, the rate of graphitization in the new heat-affected zones may be reduced considerably. If the estimated safe operating life exceeds the planned operating life of the steam power system, the rewelding procedure may well be the most economical.

Replacement of Pipe or Valve Sections

In pipe or valve materials which are very susceptible to graphitization and which show graphite in the pipe or valve metal as well as serious graphitization in the heat-affected zone, it may be advisable to replace completely the graphitized components. Bend specimens which fail at an angle of less than 15 degrees usually indicate that the degree of graphitization is extremely severe.

Where pipes and valves are replaced, the use of 1/2 Cr - 1/2 Mo, 1 Cr - 1/2 Mo or 1 1/4 Cr - 1/2 Mo materials should be considered. The replaced sections are not likely to give further graphitization troubles. Little or no further sampling is required. Moreover, improved design and fabrication practice of present-day piping and valve systems results in lower pressure drops and higher quality joints so that higher efficiencies and lower maintenance can be obtained.

RECOMMENDING REHABILITATION

Rehabilitation by (1) solution heat treatment, (2) removal of graphitized area in heat-affected zone by (a) partial or (b) complete grooving out and rewelding or (3) the replacement of graphitized pipe or valve sections is usually advisable where the degree of graphitization is found to be heavy, severe or extremely severe. Because the most suitable method varies with each particular steam power system, a definite recommendation cannot be made on the basis of a laboratory examination alone. The proper method can be determined only after a careful review and evaluation of the economic and operational factors such as operating and peak temperatures and pressures, cycling, thermal or mechanical fatigue and shock conditions, expected service life, retirement of the particular steam power unit, etc. The overall condition of the whole steam power unit must be considered also. If many joints show "heavy" graphitization, it may be advisable to cut out completely the respective weld joints and heat-affected zones as illustrated in Fig. 11. Where only one joint shows "heavy" graphitization, partial grooving out and rewelding may be sufficient.

For the purpose of illustration only, example recommendations are given below for a particular steam power system. The following operational characteristics are assumed for this hypothetical installation:

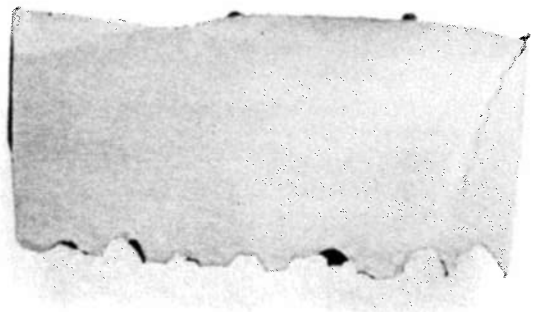
total operation	100,000 hrs.
expected future operation	150,000 hrs.
operating temperature	890 - 915° F.
operating pressure	970 - 980 psi.
shut-downs	2 per year
conditions for severe thermal shock	negligible
exposure to mechanical vibrations	negligible
piping material	carbon-moly (ASTM A206)
deoxidation practice	2 lbs. aluminum per ton of steel
pipe size	12 in. nom. (12 3/4 in. O.D.)
wall thickness	1.3 in. (schedule 160)

The following recommendations might be made:

Degree of graphitization	Recommended rehabilitation
none	take another weld-probe specimen after 20,000 - 30,000 hrs. of service.
mild	take another weld-probe specimen after 8,000 - 10,000 hrs. of service.
moderate	gouge out (partially) heat-affected zone and reweld.
heavy	cut out (completely) heat-affected zone and reweld.
severe	replace respective piping or valve materials at next scheduled shutdown. Check affected materials for cracks.
extremely severe	present condition of material extremely hazardous. Check for cracks, make immediate repairs and replace materials as soon as replacement sections can be obtained.

Where a system is subject to severe thermal or mechanical shock, the above recommendations might include radiographic and magnetic particle inspection of the steam power system.

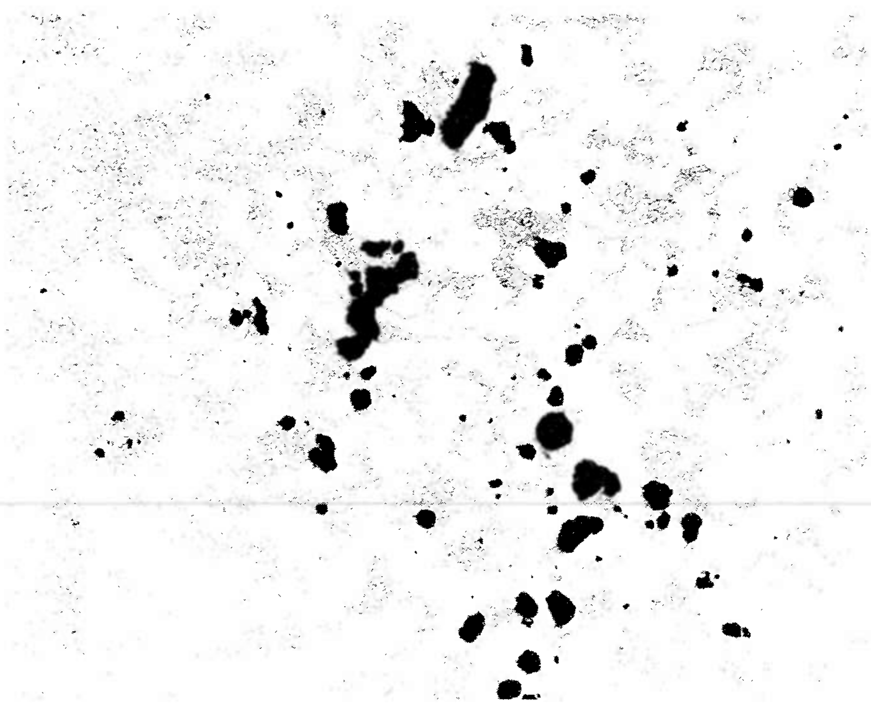
Pipe



Valve

Fig. 1. Crack in graphitized zone on valve side of "weld-probe" specimen in valve-to-pipe joint. (Because of dimensions of valve, the specimen was removed by drilling out.)

Heat-affected zone



Base metal

500X

Fig. 2. Photomicrograph of the graphitized zone in the cracked valve material shown in Fig. 1.

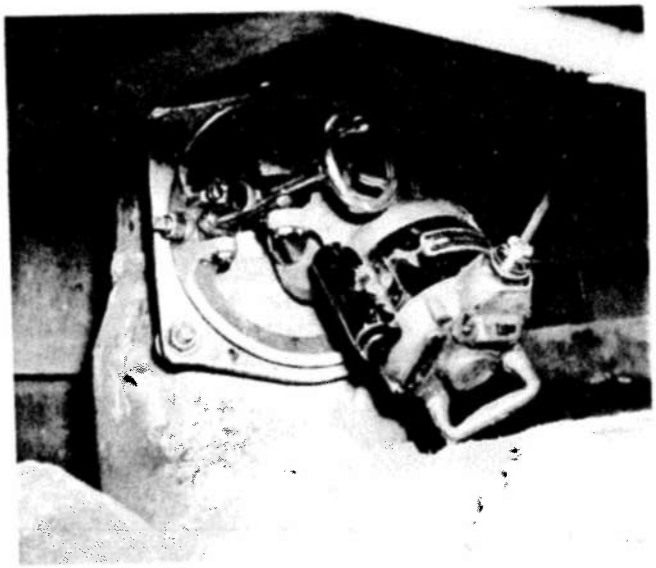


Fig. 3. "Weld-prober" saw in operation removing boat-shaped specimen from pipe-to-valve joint.

Fig. 4. Appearance of piping after removal of boat-shaped weld-probe specimen from pipe-to-valve and pipe-to-saddle joints.

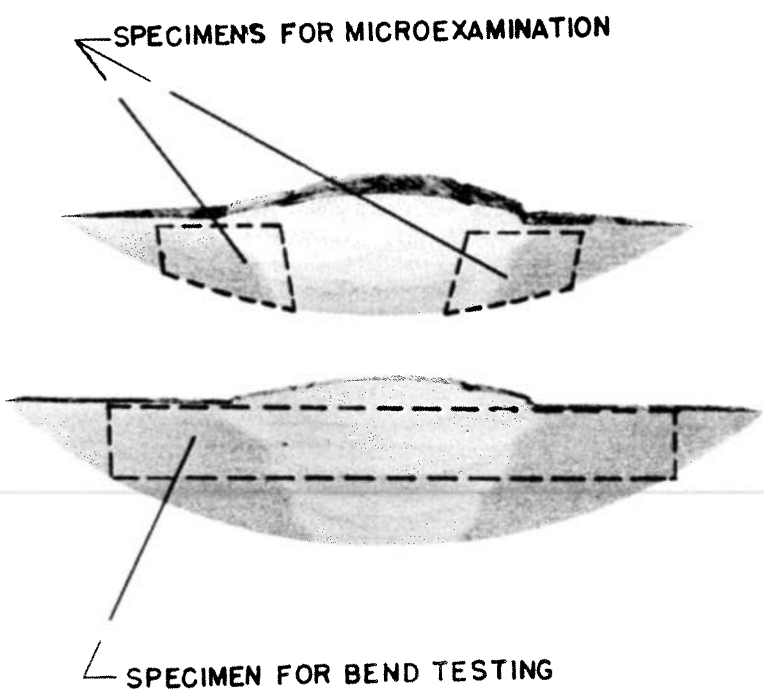
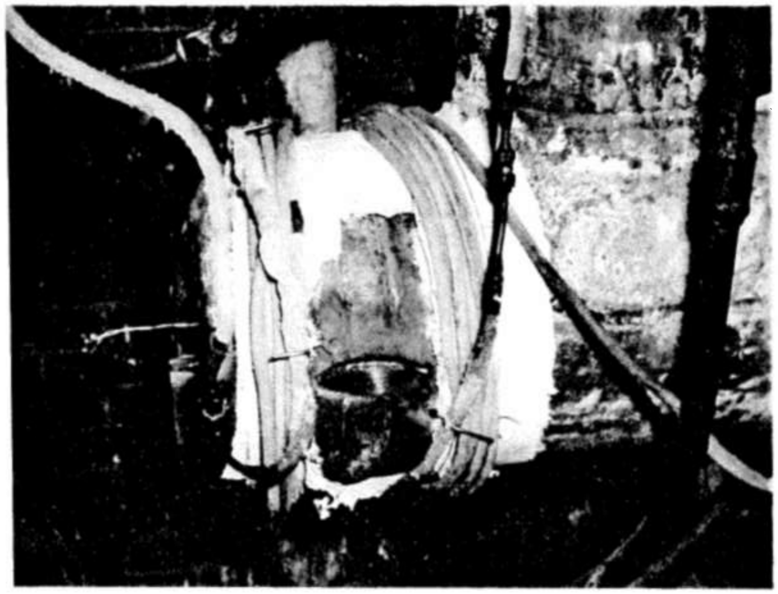
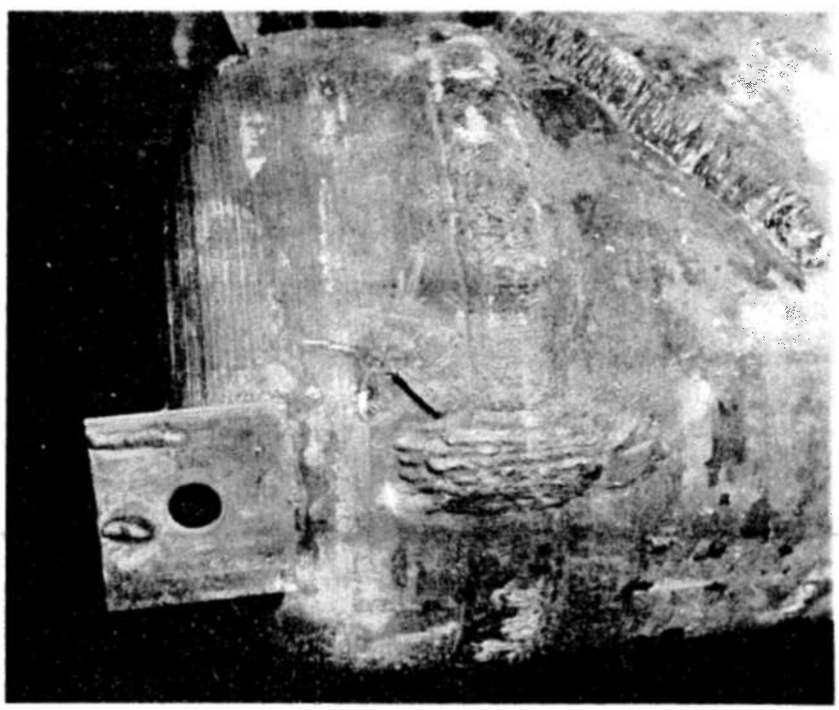


Fig. 5. Sections for bend testing and metallographic examination.

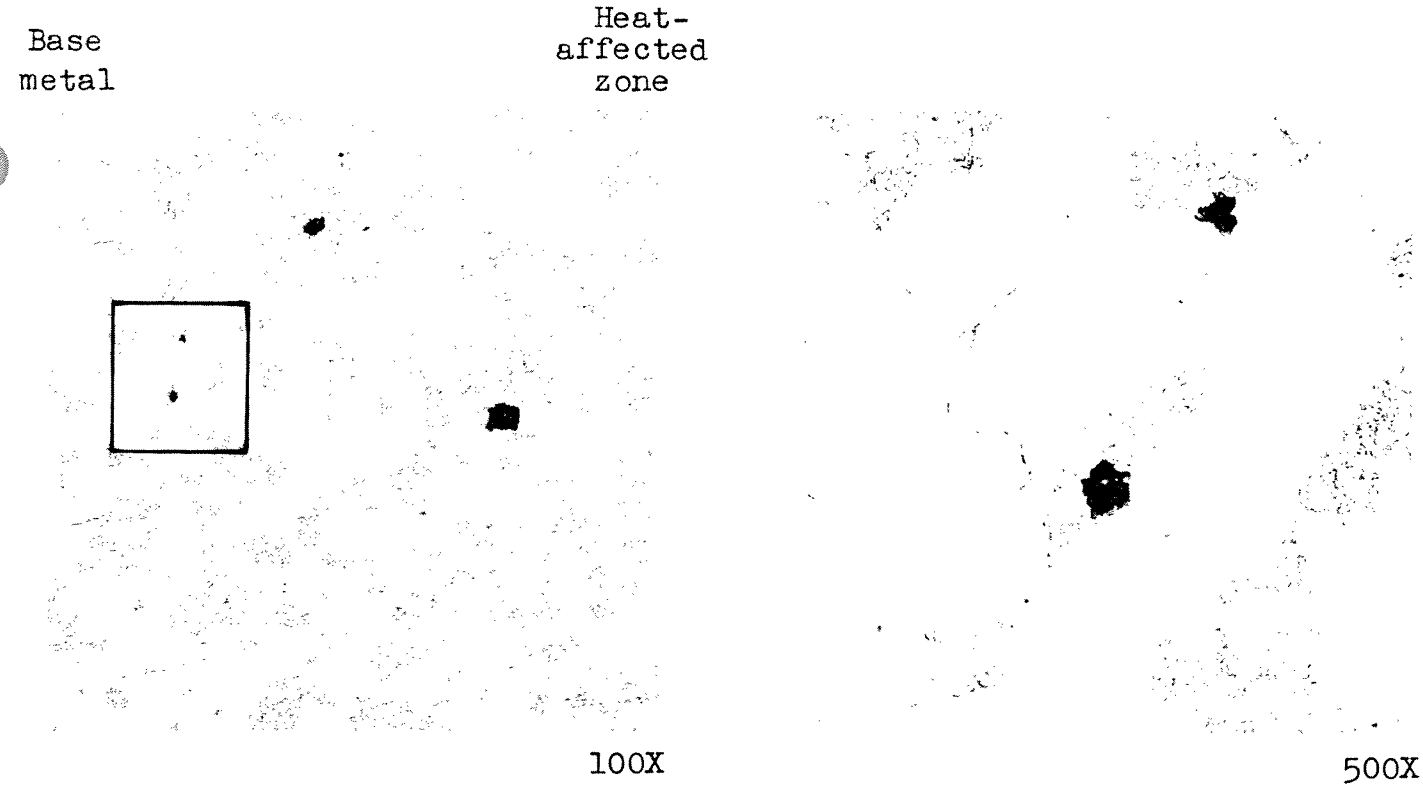


(a)

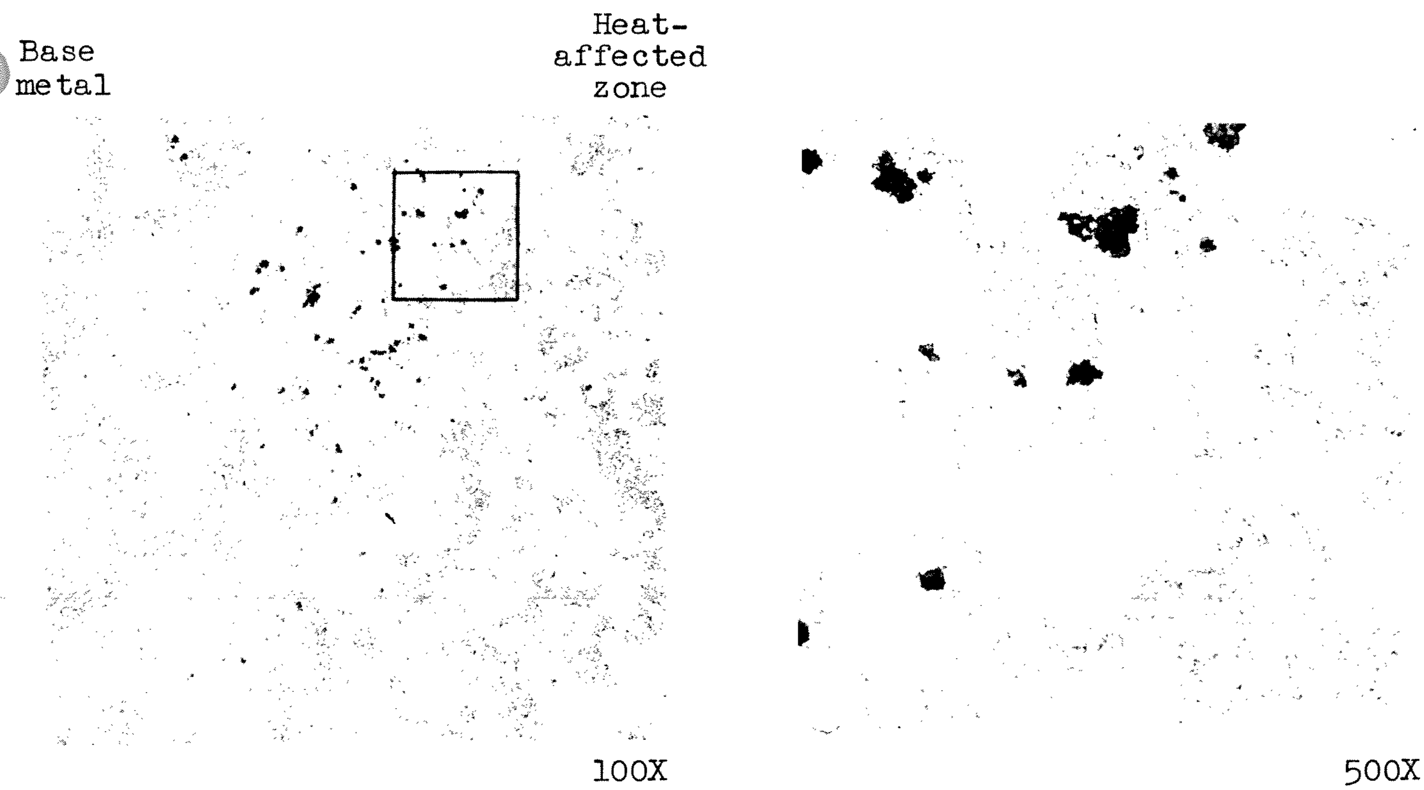


(b)

Fig. 6. Rewelded area of sampled cap-to-header joint in steam header (a) with preheating coils and deposit of initial root pass, (b) completed weld (which has been stress relieved).

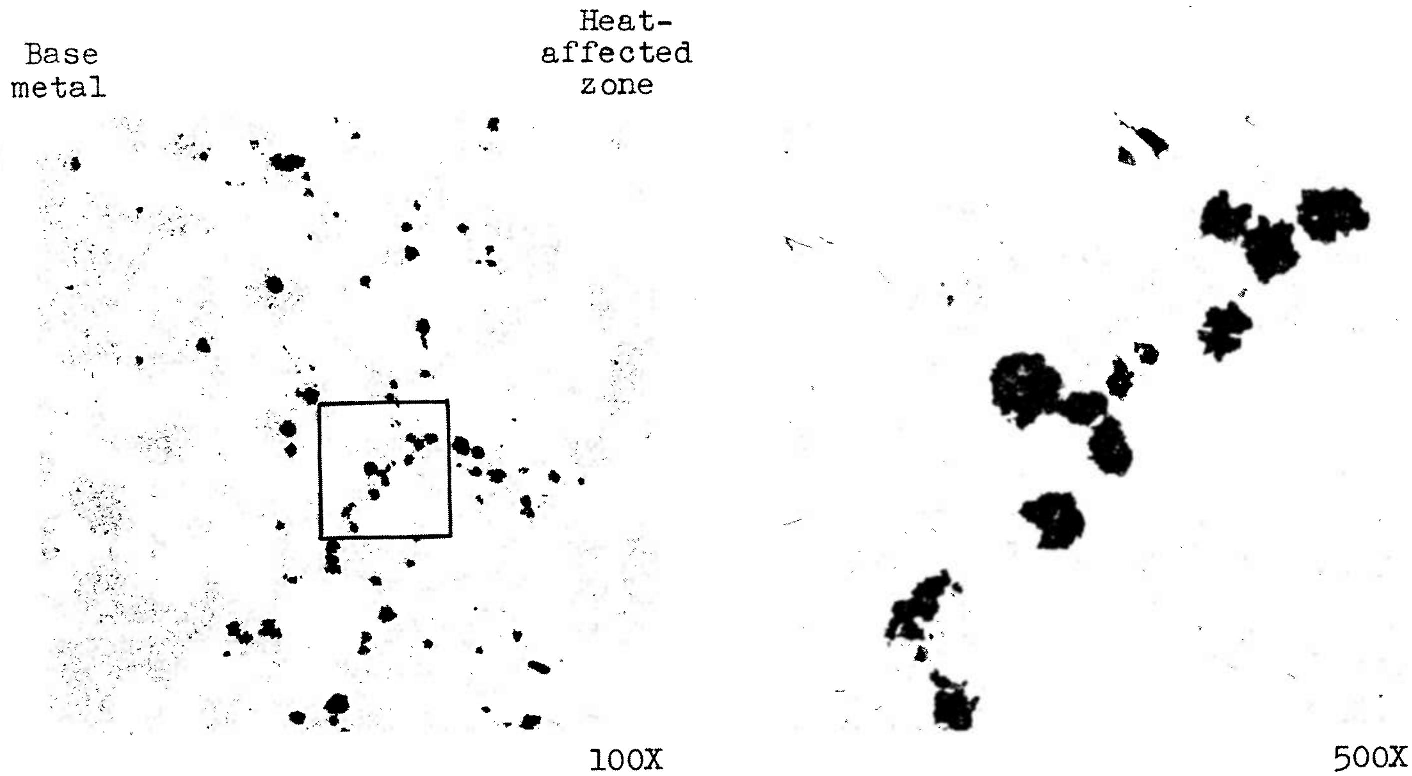


(a) "Very mild" graphitization

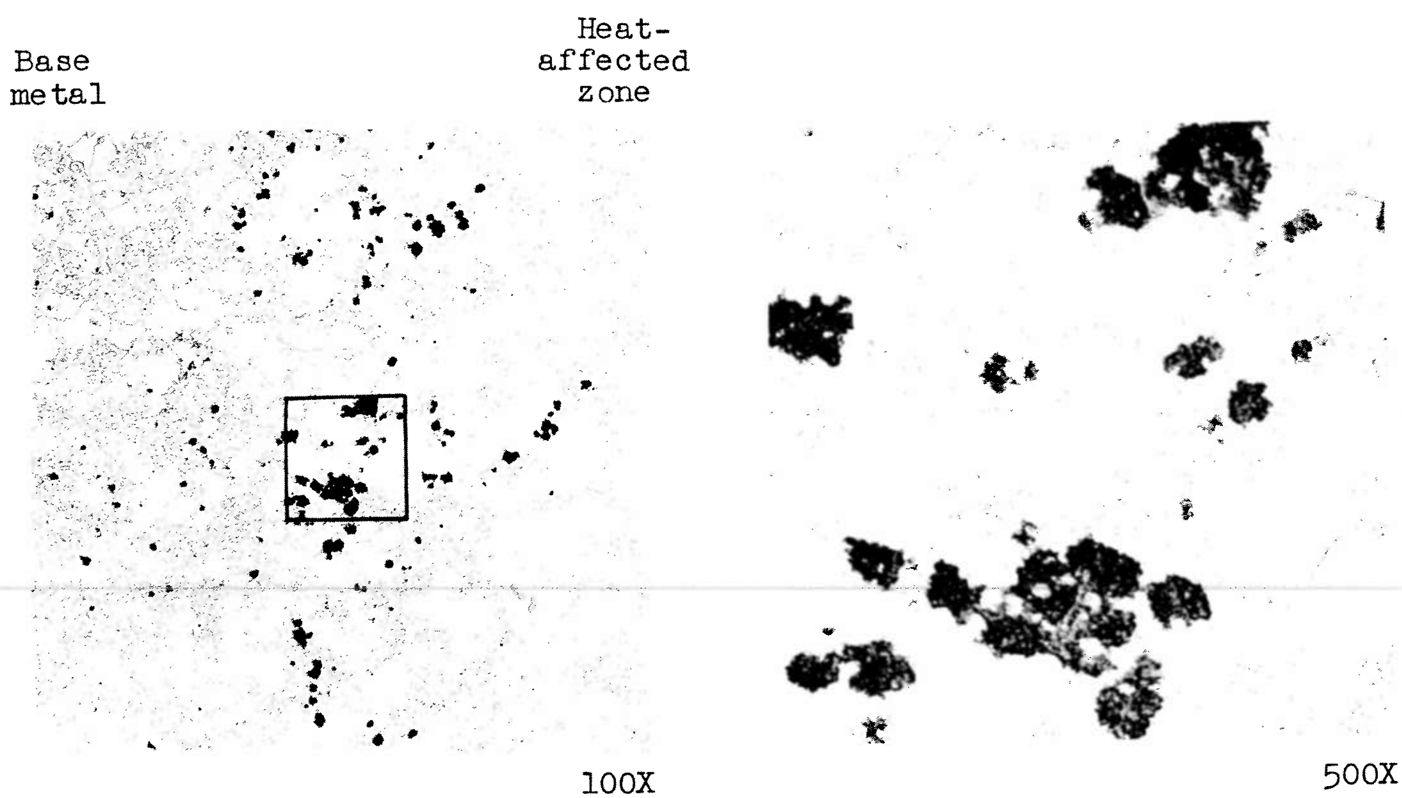


(b) "Mild" graphitization

Fig. 7. Microstructures at 100 and 500 diameters illustrating various degrees of graphitization.

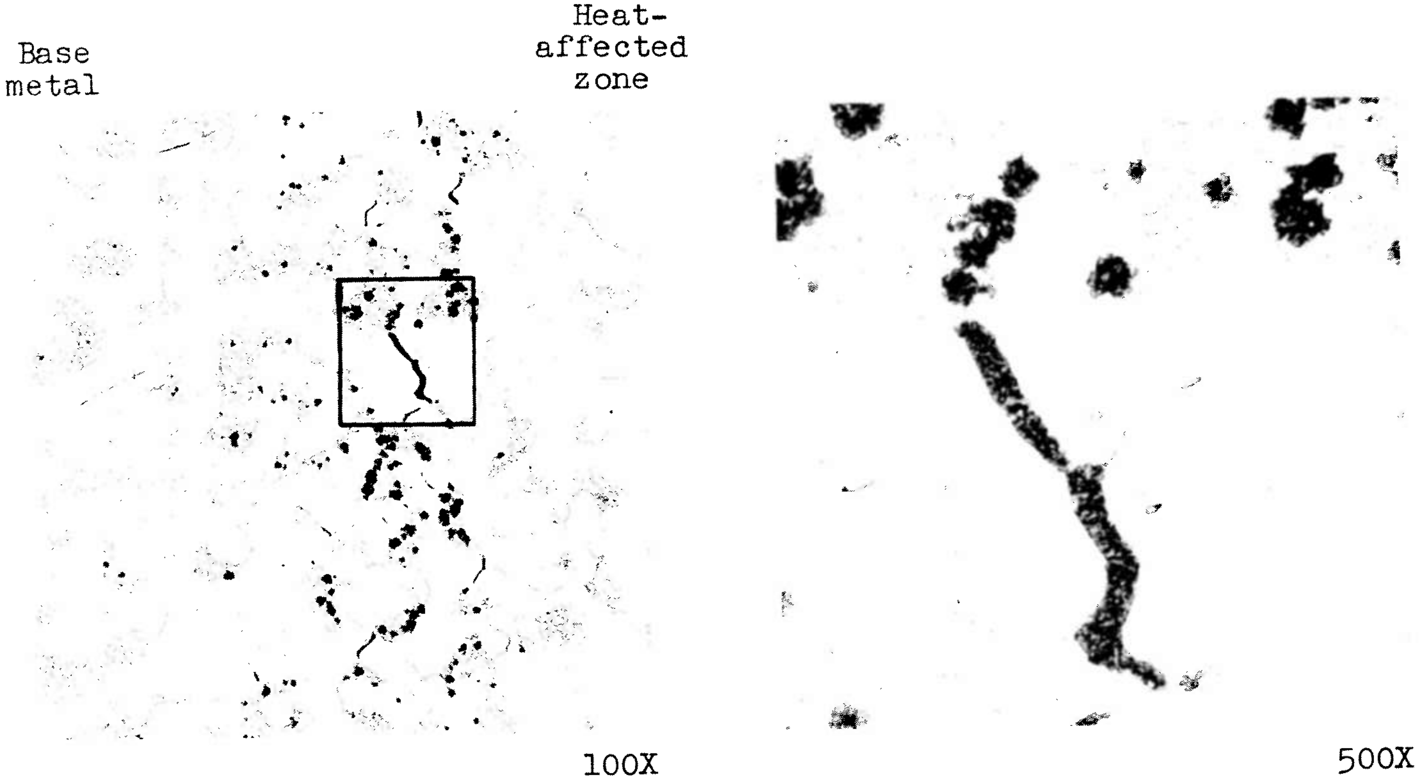


(c) "Moderate" graphitization

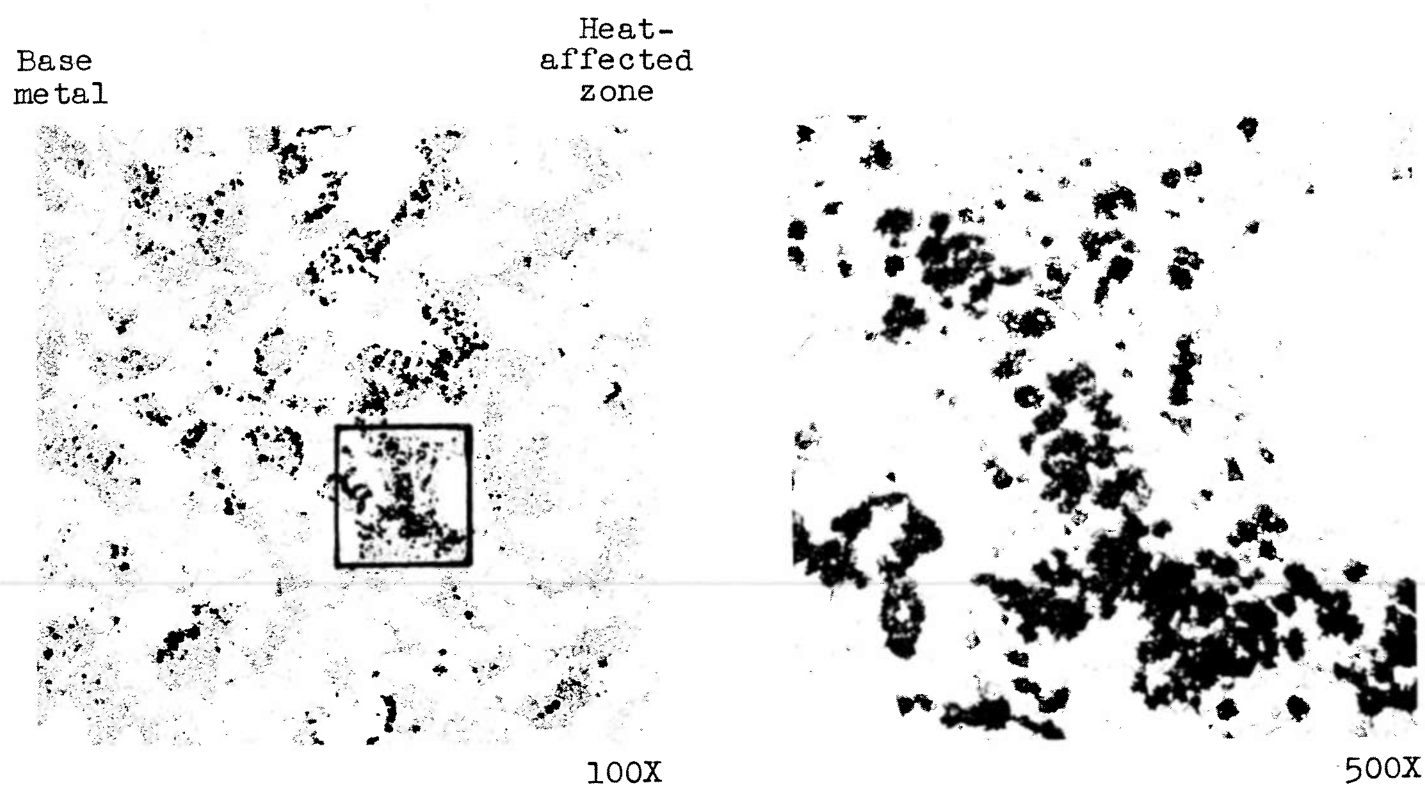


(d) "Heavy" graphitization

Fig. 7. Microstructures at 100 and 500 diameters illustrating various degrees of graphitization.



(e) "Severe" graphitization



(f) "Severe" graphitization

Fig. 7. Microstructures at 100 and 500 diameters illustrating various degrees of graphitization.

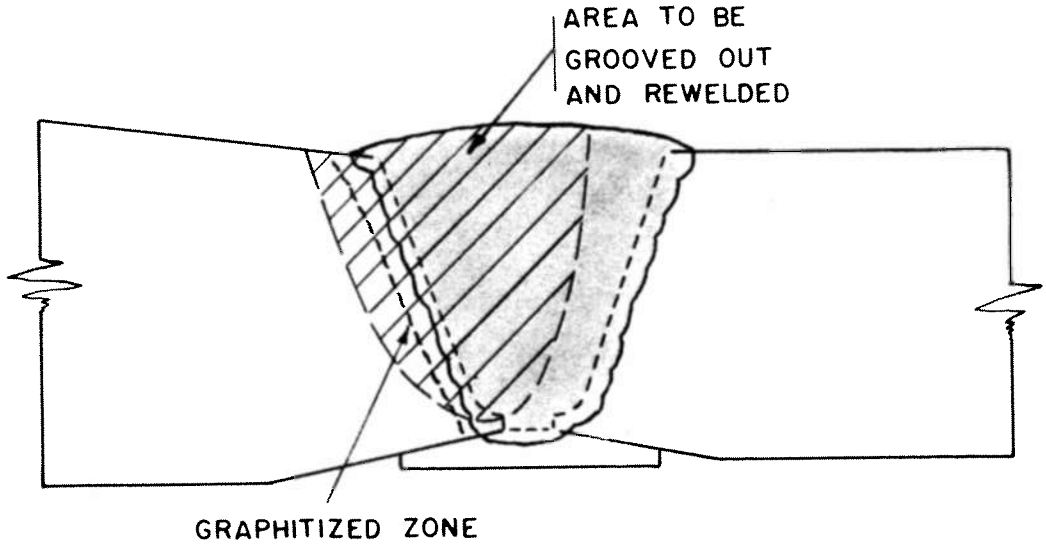


Fig. 8. Sketch illustrating procedure for partial grooving out and rewelding of joint with graphitization on one side of the weld.

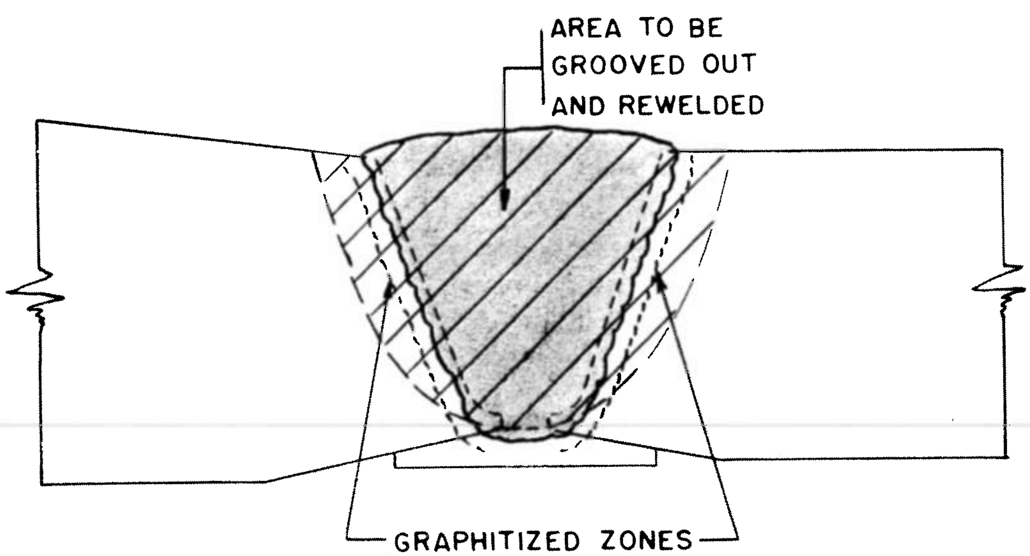
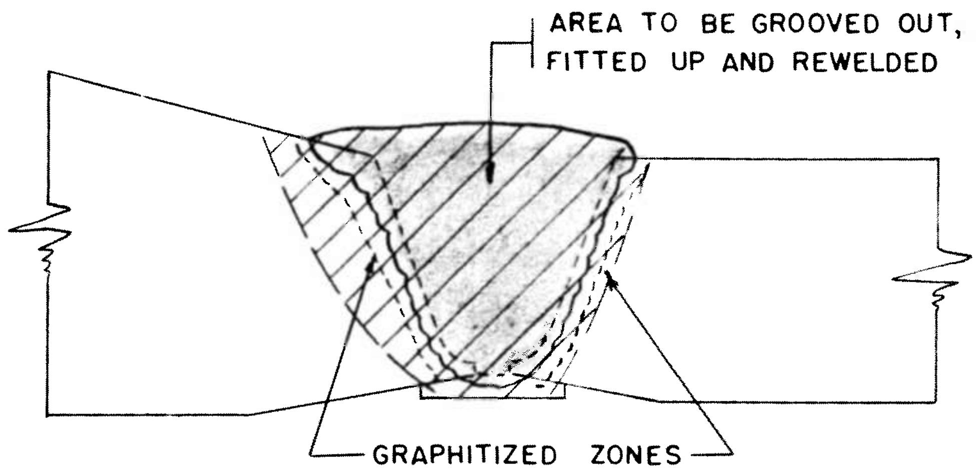
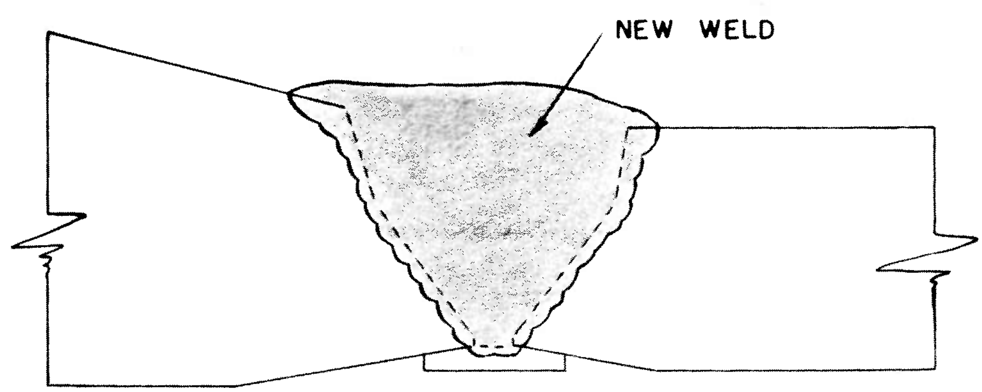


Fig. 9. Sketch illustrating procedure for partial grooving out and rewelding of joint with graphitization on both sides of the weld.



(a)



(b)

Fig. 10. Sketch illustrating procedure for complete (a) grooving out and (b) rewelding of joint with graphitization on both sides of the weld.

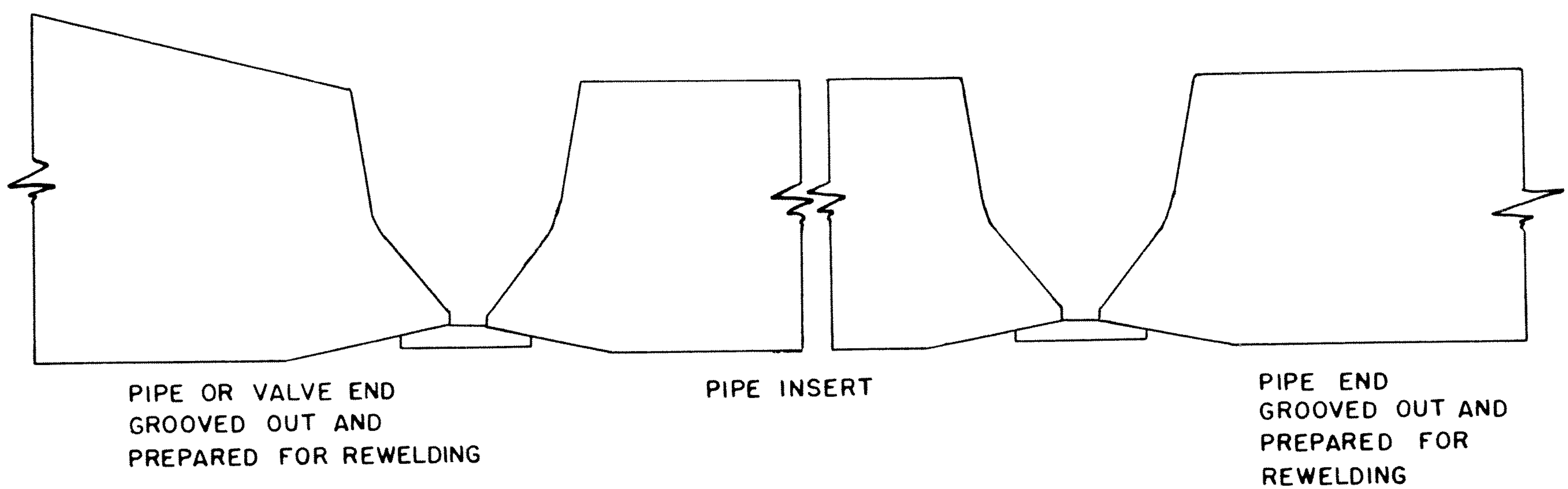


Fig. 11. Sketch illustrating inserting of pipe section to compensate for several weld joints completely grooved out, pulled together, fitted-up and rewelded.

GRINNELL'S SERVICE

In plants where the degree of graphitization is found to be sufficiently severe to merit consideration of one of the rehabilitation treatments, it is advisable to evaluate in conference with qualified engineers the best possible procedures. Grinnell engineers, with over ten years of laboratory and research experience, are highly qualified and prepared to provide each utility with this complete metallurgical service. Where desired, this service can include the recommendation and ordering of replacement materials, preparation of specifications and any other necessary engineering service.

The consulting service is available for a particular project, or for a continuous "watchdog" program in which weld-probe samples are removed periodically every 5,000, 10,000 or 20,000 hrs. and a report is made on the level of operating safety of the piping system.

A highly trained and experienced field force is also readily available and well equipped for all types of sampling and rehabilitation treatments, which are made in the shortest possible time.

PRELIMINARY EXAMINATION

In the laboratory the weld-probe specimen is cut longitudinally into three pieces.

A 1/4 to 3/8 in. wide strip is cut from the 1/8 in. thick center piece to serve as a bend specimen. On the basis of these preliminary test results, the power plant or refinery management is informed. Where a bend specimen has indicated extremely severe graphitization, the management is informed by telephone. Otherwise, the preliminary report reassures the plant that the system can be safely operated.

Under ordinary conditions, the results of the preliminary examinations are communicated to the customer within one week from the receipt of the specimens in the laboratory.

FINAL EXAMINATION

One of the side sections, cut from the original weld-probe specimen, is further sectioned to secure a small area across the heat-affected and fusion zones. The other side section is properly identified and filed for further reference.

The two "sub-sections" are mounted, polished and etched for examination under the microscope. Photomicrographs are made of areas representing the average structure and, where encountered, of severe cases of graphitization.

In a few cases a further study of the base metal is desirable and suitable sections may be prepared for microexamination.

FINAL REPORT

In the final report, the results of the preliminary and final examinations are reviewed and correlated. Where applicable, recommendations are given for future "weld-probe" programs and/or for consideration of rehabilitation programs of graphitized steam power systems. All recommendations are supported by test data and photomicrographs.