HIGH PRESSURE RESEARCH AND APPLICATIONS IN THE BELGIAN INDUSTRY

Louis Deffet
Institut Belge des Hautes Pressions, Sterrebeek, Belgium

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by

Dr. Louis DEFFET[x]

INTRODUCTION

"The fact that the pressure influences the chemical reactions on which industrial processes are based, was known later than the same one referring to the influence of the temperature and both facts have nowadays to be attached the same importance to. In fact, our industry has consequently made considerable progress in the field of the synthesis and mass production, which events stand out as landmarks in its history since the beginning of this century". These are the first sentences by which Professor L. Jacqué begins one of these remarkable editorials, which are published each month in the french review "Chimie et Industrie".

In Belgium, and there perhaps more than in foreign countries, the chemical industry has since a long time made use of the high pressures for extending the scope of their activities and valorizing their products: therefore the most important applications of the high pressures which above mentioned editorial calls back to the reader's memory are applications in which this country as well as France are greatly interested.

(x) Director, Institut Belge des Hautes Pressions, Sterrebeek (Belgium).

But owing to the constant development of the engineering science, the Belgian industry must spare no effort to keep abreast of the times. The Belgian Institute for High Pressures (Institut Belge des Hautes Pressions) endeavours to give this industry an effectual support by studying and solving the new problems with which the latter is confronted, which support is rather restricted, owing to the force of circumstances.

This report aims at showing how and by which means this Institute fulfils its task, which is always a difficult but often an exciting one.

Ample funds are not made available in Belgium for research as it is the case in the U.S.A. and in some Belgium's powerful neightbour countries. Therefore the specialized laboratories must be extremely well equipped, before engaging in scientific activities relating to a particular field of the engineering science. Suggesting or accepting to do research work is a thing which wants thinking over, because the less important, the funds available to this purpose are, the more difficult and the narrower is the way to follow with a view to obtaining the anticipated results.

These notions, which we deemed to call back to the memory of the readers of this report only aim at answering a question which certainly will be put by said readers, who will not understand why such an Institute of a rather moderate size engages in a lot of scientific activities into many fields instead of selecting a particular field. As paradoxal as it may be, it was necessary to adopt this policy, because the results of the research work done in the field of the high pressures have to be made use of in Belgium by a lot other laboratories.

These results will however show, that such a policy pays.

I. RESEARCHES ON ELASTICITY AND PLASTICITY OF METALS AND STEEL.

A. BEHAVIOUR OF THICK-WALLED CYLINDERS, SUBJECTED TO PRESSURE.

1. Foreword.

When examining the circumstances, which cause thick-walled cylinders to break, because the stresses to which they are subjected exceed the elastic limit, we have observed a phenomenon which is hardly known and of which an accurate description has not yet been given. We mean to say the relative thickness of the walls and its influence upon said circumstances.

In fact, we have been able to ascertain various facts which had not yet been established or wanted to be confirmed by the experience (cracks appearing on the inner or on the outerside of the tube, ductile strain of the metal leading to its rupture, values of the pressure corresponding to the elastic limit of the metal) but we also could observe that the ratio of the outside diameter of a cylinder to the latter's inside one passes through a critical relative value.

This is an experimental fact of which the cause has not yet been found and which deserved to be carefully examined, because it may have far-reaching consequences from the technical point of view. It has been indeed observed that a thick-walled tube does not necessarily withstand the pressure better than a thinner one and that as far as certain grades of steel are concerned, the resistance of the tubes to pressure decreases as the thickness of the wall exceeds a certain critical value. Supposing that cylinders are tested in following circumstances, the ratio of the outside diameter to the inside one being constant and in the present case being equal to 2.2, supposing too that said diameters are gradually increased, it is obvious that the thickness will increase in the same proportion too, but beyond a critical value of the wall thickness, we will observe that the elastic

limit, recorded outside the cylinder by means of electric extensometers as well as the pressure corresponding to the breaking strength of the material, of which said cylinder is made, will decrease too. The following values obtained by making experiments with cylinders made of a half mild steel are extremely typical in this respect (table I).

Table I.

Temperature °C	Diameter (mm) ~~ou~~tside *in*	Diameter (mm) ~~in~~side *out*	Pressure in kg/cm2 Beginning of plasticity	Pressure in kg/cm2 Rupture
20	17.5	38.5	1 750	4 000
	20	44	1 850	4 100
	20	44	1 850	4 200
	23	50.6	1 550	3 700
	23	50.6	1 350	3 800
30	17.5	38.5	1 850	4 800
	17.5	38.5	1 750	4 800
	20	44	1 850	4 800
	23	50.6	1 450	3 700
	38.6	85	1 300	3 200
	45.3	99.7	900	2 500
50	17.5	38.5	1 900	4 600
	20	44	1 850	4 900
	23	50.6	1 450	3 600
200	17.5	38.5	1 900	4 700
	17.5	38.5	1 850	4 700
	20	44	1 450	4 900
	20	44	1 550	4 900
	23	50.6	1 650	4 600
	23	50.6	1 450	4 600

Such observations had not yet been the subject of an accurate description. By testing high pressure apparatuses, other research workers had however observed breakages which could not be accounted for, neither by the calculations nor by the experiments hitherto made. Accidental causes have been brought forward for explaining such breakages which have been rarely inquired into and it seems that the scale effect has never been correctly brought to light (1, 2).

As the study of the materials strength is not the chief object of our researches, we did not devote at this time a lot of time for more carefully studying the particular aspect of the problem of the thick-walled cylinders. This question was later on discussed again and in 1960 it was decided to set up a committee for studying the thick-walled cylinders, which committee was presided over by the late Professor L. Baes. This committee came to the conclusion that:

1° The research work relating to the thick-walled cylinders should not be discontinued and that the relevant experimental data should be determined under the best conditions by refining the methods for measuring them and by taking the necessary precautions for correctly making the pieces to be tested to that purpose;

2° There was a problem of a much wider significance, this problem consisting in distinguishing the circumstances themselves, which are responsible for the steel, breaking when it is in a state characterized by the presence of three axes, these circumstances being of such a nature that they would help us to understand better how the steel breaks when it is in a state characterized by the presence of one, two or three axes. This leads the research worker to consider that the fundamental problem of the metal breaking strength may be studied by means of tubular test pieces, the tubular form being apparently the simplest one which can ever be met in this field of the engineering science.

Consequently, if the problem of the scale effect is certainly a problem which deserves to be carefully studied and of which the study should not be discontinued, there is an other problem which is

not less interesting, this problem consisting in making use of tubular test-pieces for studying the fundamental problems pertaining to the breaking strength of the different grades of steel.

2. Scheme of the research work.

The first part of this scheme was carried out from October 1960 to the end of December 1961. It consisted in experimental works done in the laboratories of our Institute and also in the problems being approached by the research workers of the Metallurgical Research National Center and carefully examined by them on the basis of theoretical considerations, and in making the most of the results obtained.

The execution of the second part of this scheme started in 1962 and will be completed in 1965. The experiments have been carried out by applying the same methods as those applied for carrying out previous works, these methods essentially consisting in carefully examining the behaviour of thick-walled cylindrical test pieces subjected to inside hydraulic pressures with a view to showing how these pressures vary with the elastic limit and the tensile stresses to which the steel grades tested are subjected.

With a view to obtaining results, which are beyond question following rules have been strictly complied with:

a. As regards each type of steel to be examined, the test pieces have been strictly taken from the same lot, this with a view to eliminating errors which may come from slight differences in quality between said test pieces.

b. The cylindrical test pieces have been carefully made and subjected to a slight, well defined heat treatment, after they have been made. Their length was nearly equal to 4 outside diameters, the ratio of the outside diameter to the inside one being 1.5 and 2.

c. The measurement of the strains has been made at the outer side of the tube and in some cases, at the inner side of the same. These measurements have been made by means of an apparatus measuring the strains at ten places that is to say by means of strain-gauges sensible to one millionth (i.e. a microdeformation).

d. The pressures have been measured by means of a manometric balance sensible to 0,5 thousandth.

As regards the different grades of steel, the dimensional effect of the thickness of the walls upon the circumstances under which the strains are no more elastic ones and upon the circumstances under which the steel breaks has been carefully determined. To this purpose :
a) the ratio of the outside diameter to the inside one (k)
b) the thickness of the walls
have been varied, said ratio k being kept constant.

3. Experimental researches.

a. General measurements.

The tests carried out up to now, related to a soft steel and a half hard steel. They been carried out by using test- pieces with different values of the ratio $\frac{\text{outside diameter}}{\text{inside diameter}} = \frac{de}{di} = k$ and for each of these ratios, with different thicknesses of the wall. Said tests have been carried out at the ambient temperature and at different temperatures, below the ambient one: namely -20°, -40°, -60°, -80°C. In the course of these tests, the pressure under which the plastic deformation reaches the extrados (p_e) has been determined as well as the maximum pressure to which the test-piece was subjected before breaking (p_m). The résults of these tests are classified in the figures 1 to 3. The three first figures show the influence of the thickness of the wall at the ambient temperature and at the temperature of -80°C for cylinders of which the diameters ratio k is equal to 2 and 1.5.

Fig. 1 shows the influence of the temperature for a half hard steel, said ratio k being in this case equal to 2 and the thickness of the wall equal to 8 mm. Fig. 2 makes a scale effect apparent as regards the soft steel, because the pressure p_e as well as the pressure p_m slightly decrease when the thickness of the wall increases. As regards the half-hard steel, the pressure p_e varies in the same direction, but p_m varies in the opposite direction, which means that it increases as the thickness of the wall increases. Fig. 3 shows a scale effect without anomaly as regards the cylinders, for which k is equal to 1.5.

b. Measurements of the deformation.

1. Each tested cylinder had been provided with a certain number of strain gauges, adhering to its outer surface so that the circumferential and longitudinal deformations could be measured at any time, during the test. As regards the first series of soft steel cylinders of which the diameters ratio k is equal to 2, one has studied how the circumferential deformation varies with the pressure. This study mainly aimed at examining if it was possible to detect the moment when the plastic deformations set in at the intrados, on the unique basis of the deformation measurements at the extrados. The deformations, resulting from theoretical calculations applying to the extrados, have been compared on the assumption of a plastic deformation progressing by concentrical layers as shown on fig. 4; with the deformations measured in the particular case of a cylinder, for which the experimental data had been made available in the greatest number. This comparison shows that the assumption of a plastic deformation progressing by concentrical layers leads to deformations definitely smaller than the real ones (nearly 50 times smaller). This result suggests that the real deformation is not progressing by cylindrical layers, but is rather connected to more localized deformations of a

bigger amplitude, of which the mechanism is similar to this one relating to the Lüders bands, appearing in the course of the tensile test, as shown on figure 5.

The problem of the scale effect is consequently connected to the progression of these bands plastically strained. In the tensile test, the stress condition is the same at each point of the test-piece and the Lüders bands grow without difficulty, whereas the tensile stress is kept constant. On the contrary, in the cylinder subjected to a lower pressure, the stress condition continuously changes when passing from the extrados to the intrados. A Lüders band appearing at the intrados and showing a tendency to progress towards the extrados meets than stress conditions less and less favourable to its progressing and is rapidly stopped. It will continue progressing in this direction only after the inside pressure has been increased. The progression of the Lüders bands slowed down by the stress conditions characterizing the outside layers of said cylinder could account for the scale effect observed, when the plasticity state sets in. In fact, it has been observed that, when two cylinders geometrically similar are subjected to the same inside pressure, the gradient of the stresses is higher in the small cylinder. It can reasonably by expected that the progression of the Lüders bands is better slowed down in this cylinder and that it will be necessary to apply a higher pressure with a view to obtaining that the plasticity state sets in.

2. The measurements of the deformation, made on the first series of soft steel cylinders of which the diameters ratio k is equal to 2 have thus shown that it was possible to obtain a valuable information by making use of the measurement deformations at the extrados. Taking this possibility into account, one has made deformation measurements greater in number, which have been systematically utilized by dividing the deformation measured, by the pressure reigning at this time in the cylinder and be graphically showing how this ratio varies. So long as

the deformations remain purely elastic ones in the whole cylinder, the ratio obtained by dividing the deformation by the inside pressure remains constant. The variations of this ratio show thus the possibility of disclosing any anelastic or plastic behaviour of the cylinders.

c. Interpretation of the results obtained.

Briefly, we observe in all the cylinders examined that an anelastic behaviour of the metal appears as far as lower pressures are concerned, when the stress to which the metal is subjected exceeds the elastic limit at the intrados. When we compare different cylinders, geometrically similar together, we observe that the aspect of this anelastic behaviour varies with the thickness of the wall. The differences shown by cylinders for which the ratio k is the same, are connected to the scale effect appearing when the plasticity state sets in. On the other hand, it is highly probable that the anelastic behaviour of the cylinder is in fact due to microdeformations, that is to say to a phenomenon which is actually carefully studied by the Metallurgical Research National Center in the case of the "one-axis traction", said phenomenon being due to small displacements of the dislocations in respect of their "Cottrell clouds".

d. Such a study has been conducted with an other one of a more technological character namely a study of which the results will be explained on the basis of the results already known and of those, which will be obtained after carrying out tests on smooth test-pieces.

In the course of the present study, it is suggested to study the transition phenomenon on one type of cylindrical V notched test-piece. The attention of the research worker shall be particularly drawn to carefully studying the test-piece during its breaking but in addition to this, said test-piece shall be in certain cases subjected to a test, carried out by means of extensometers.

The aim of these tests is to classify the steel grades according to their transition temperature, this by using cylindrical test-pieces, which has not yet been done.

The results of the series of tests will provide the constructors with a valuable technical information. In fact, the development of the equipment working under pressure, entirely depends upon the state of our scientific knowledge as regards the passage to the plasticity state of the metal and the behaviour of the metal during its breaking. In fact, the criteria used to this purpose do not take into consideration the gradient of the stresses and should be improved. Besides, the brittleness of the metal at the low temperatures should be carefully studied because the extension of our knowledge about it is a thing in which the builders of cylindrical equipment and the builders in general are most interested.

Here is an example of a series of tests now in progress (table II). The values of the transition temperatures measured on one side, on a test-piece subjected to the notched bar impact test (Charpy V notch test) and on a cylindrical test-piece provided with the same type of notch are shown hereafter in tabular form.

Table II.

Test temperature °C	Rupture pressure kg/cm2	Brittle structure %
− 0	2 640	0
−10	2 660	2
−23	2 700	10
−33	2 760	27
−40	2 790	38
−50	2 810	45
−60	2 980	73
−70	3 100	85

B. IMPROVEMENT OF MANOMETERS.

In the course of these last ten years, we have considerably improved the metallic membrane and tube manometers. To this purpose, we have done a lot of research work in this field, which research has been the subject of numerous reports, published in the technical periodicals and leads to this result that the hysteresis phenomenon no more affects the measurement of the pressures and that the manometer can be used during its normal life without accertaining any displacement of its zero. Besides, our Institute has worked out precise methods for testing the manometers, which manometers have been consequently standardized and granted a quality mark distinguishing the manometers of the different types.

We became then aware of the fact that a lot of research had to be done, regarding other types of manometers particularly the manometers, used by the petroleum-industry and that we must endeavour to reduce to the minimum the troubles to which the mechanism of normal manometer is subjected when these manometers are normally used.

In fact, the manometers used by the petroleum-industry are subjected to very severe tests which consist in subjecting the tubes to be tested, to a pressure, which varies between zero and a predetermined value, the pressure changes occurring a very high number of times. According to the American standards, the number of said pressure changes amounted to 2 500 000. It has been ascertained in the U.S.A. as well as in the course of our carrying out appropriate tests, that these standards were really too severe. We have tried improving the American testing method so as to give satisfaction to the petroleum-industry. We were not successful in doing so because the testing cycle could not be defined with precision. This accounts for our observing variations in the quality of the tube, even breakages which occured under conditions which in the present state of the engineering science remain unexplained.

Therefore, we requested the cooperation of the Belgian manometers manufacturing industry with a view to more carefully studying the problem of the manometric tubes.

The elastic strain of the manometric tubes is expressed by different formulae, which appear to be contradictory, because the problem has to be simplified, owing to the complexity of the phenomena involved, which simplifications are such, that each formula suggested is applicable within very narrow bounds, which cannot be clearly defined.

Consequently a great number of experimental measurements have to be made with a view to condensing their results in one or several formulae, which would permit of predetermining the size of the tubes of which the use is most apt to solve the technical problems with which the industry is confronted.

Research work in this direction has been done in Great-Britain on a semi-theoretical and semi-empirical basis, but this work is too incomplete as regards the bounds within which the formula discovered is applicable. Without these bounds, the errors made by applying said formula are quite unacceptable.

We have however based on this British research work our own researches in the same field. We have measured and compared together a lot of manometric tubes, classed into several groups and for which the deformation laws are not to complex ones.

1. category : tubes of an elliptic section or of which the section is nearly an elliptic one.
2. category : tubes of an oval section or of which the section is nearly an oval one.

In each of these categories, we have distinguished the sections of which the size is bigger, from those of which the size is smaller:

a) 17 x 8 mm
b) 12 x 4,5 mm
c) 7 x 3,5 mm.

We have thus obtained six classes including all the types of tubes studied. In each class and by taking into consideration the maximum number of tubes, we have determined the four coefficients which are most appropriate for being introduced in the formula of which the use is recommended by author:

$$\zeta = K \frac{P}{E} \frac{R}{B}^{m} \frac{A}{B}^{n} \frac{A}{t}^{q}$$

that is to say K, m, n, q; A, B, R, t being used for determining certain dimensions of the tubes, p being the pressure and E the elasticity modulus of the material considered.

For each tube one has determined:

- the lift Z, the radius Ro, the angle Ø (which is necessary for obtaining ζ) and the angle x between Z and the tangent of the tube;
- the shape of the section of the tube by optically plotting the coordinates of points belonging to half a section (symetry as to a vertical axis);
- the expansion of the small axis for a determined pressure with a view to distinguishing the strongly strained tubes from the little strained ones;
- the elasticity modulus E (some tubes have been used for measuring this coefficient E and verifying that its value is a constant one).

For each tube one has:

- plotted the curve showing how the first displacement of the zero (up to 15 % of the stroke) varies with the pressure p;
- plotted the curve showing how the second displacement of the zero (up to 2 % of the stroke) varies with the pressure p;
- determined the force which applied to the end of the tube under an angle engenders the same deformation Z as the applied pressure p. This last quantity is a measure of the useful work of the tube, when it strains.

Tubes made of steel and phosphorous bronze of following size 150 x 17 x 8, with an elliptic section and subjected to rated pressures ranging from 0,8 to 800 kg/cm2 have been used for experimentaly taking the first measurements. Each "Bourdon" tube has been taken a maximum number of measurements so that it could be classed into the right group after examining the results experimentally obtained. To this purpose each "Bourdon" tube is taken 30 measurements which include:

- width and height of the tube at three different places (base, middle part and end)
- its thickness
- the displacement of the end the tube in the direction of both axes
- expansions and contra—ctions of the tube
- the different rotation angles carying with the applied pressure
- the plotting of the trajectory of the tube
- the variations of the curvature radiuses when the tube is used for measuring pressures.
- the force applied to the end of the tube and necessary for engendering the same displacements as those engendered when the tube is subjected to a pressure
- the value of the elasticity modulus of the material used
- the plotting of the shape of the tube section.

Most of the measurements were made by means of an optical bench, the precision of the measures being equal to ± 2,5 microns. The different angles were measured by means of a picture projector, which projects on paper the picture of the tube enlarged to a scale of 2/1. By marking the different positions of the tube, when the latter is subjected to a pressure, controlled by a manometric balances we can draw the series of lines which are necessary for measuring the different angles. By using this method, the angles can be read with a precision amounting to 30 minutes.

The section of the tubes is plotted by means of a photographic plate. With a view to eliminating any optical aberration, the impression of the sections is obtained by enlarging said photographic plate.

The Young modulus is obtained by measuring the set of a small bar, tailed in on one side and subjected on the other side to a certain force. Said small bar is taken from the tube in a direction parallel to the longitudinal axis of said tube and in the middle part of the latter. It has a triangular or rectangular section of which the size is equal to 70 x 15 mm. The results obtained by carrying out adequate tests have been analysed by the engineers of the Department "Manometers and Thermometers" of the "Compagnie Générale des Conduites d'Eau", Liège. They already show that this method is applicable to the generality of the cases and it is a method on which a new theory relating to the manometric tubes can be based.

II. RESEARCHES IN CHEMISTRY.

A. CHEMICAL REACTIONS.

The "Institut Belge des Hautes Pressions" had contemplated for years, publishing studies on chemical reactions. An experimental thermodynamics section had been consequently created not only with a view to developing and applying methods for measuring different thermodynamical quantities, as we explained otherwere (4), but also with a view to encouraging research work in the field of chemistry. The execution of this work was however delayed because shortage of buildings, suitable to this purpose, this being due to the fact that the new laboratories of the Institute were only made available in April 1963. From that moment, no effort has been spared with a view to creating the equipment necessary for successfully conducting said research work, which started in December of the same year. What this research work aims at, has been explained on several occasions and this is a thing which we now only need to mention without going into details (4).

The fields in which said research work is to be done have been determined by the requirements on the Belgian industries:

The main fields, which are now inverstigated are the following:

- Synthesis and polymerizations carried out by means of organic compounds subjected to the action of hydrogen, carbon monoxide, ethylene and methane.
- Building of fluorinated compounds.
- Polymerization by oxo-syntheses.
- Physical and chemical research work on the acetylene.

Such kind of research work is normally included in the programme of the laboratories, which study the action of the high pressures on the chemical reactions. In the present case, the selection of the reactions to be studied has been based on the researches already in progress in some Belgian laboratories and their results have not yet been disclosed as being at least up to now of a rather confidential nature. This is accounted for by the fact that our laboratory started working a little more than one year ago and consequently has not yet been in a position to successfully achieving research work of which the results are worth publishing.

The techniques, actually made use of, permit of doing research in a highly corrosive medium up to a pressure of 3000 atm approximately, at a temperature of 400°C. The volume of the reactors lies between 250 cm3 and 5 liters; they are mechanically stirred up or provided with electromagnetic stirrers.

The gases used for bringing about a chemical reaction are first compressed at a pressure of 1000 atmospheres by means of membrane compressors or by means of a piston compressor. They are then eventually compressed up to a pressure of 3000 atm by means of a supercharger separator and then led straight to the reactors or kept in stand-by containers. The pressures as well as the inner temperatures of the reactors are recorded by applying classical methods.

The reactors, superchargers and special containers are placed in adequate cubicles, which are placed too in buildings of which the walls are particularly thick. Photographs 1, and 2 show the compressors room as well as the outside of both cubicles.

The newly created section normally develops by adapting itself to the steadily increasing requirements of the industry. It is certain that the research work done in this section will be in the near future the subject of publications, dealing not only with the technical innovations of the chemical engineering science but mainly with the results obtained by successfully carrying out the chemical research work, now in progress.

B. CORROSION OF STEEL BY HYDROGEN AND HYDROGEN SULPHIDE UNDER PRESSURE.

1. Object of the tests - Experimental method.

It is hardly necessary to stress the importance of knowing how metals and alloys behave when they are in the presence of hydrogen at a high temperature and under high pressures.

Numerous are nowadays the industrial reactions, which the chemical industry can only make the most of, when alloys offering under well determined conditions the highest degree of security when being used, are made available, whereas the percentage of expensive alloying additions in the base metal is kept to a minimum.

As the ferro-alloys are among the materials which can be used to that purpose, those which most successfully combine the properties of strength and ductility at the ambient temperature as well as at a higher one, it is easily understood that the metallurgists have since a long time taken an interest in these alloys.

In fact, it is well known that the standardized carbon steel grades decarburize at a temperature exceeding 300°C or 400°C, when they are in the presence of hydrogen. Moreover, hydrogen diffuses through the metal so that the metal completely loses its ductility, because the intergranular cohesion is destroyed.

We found it interesting to know how this stability would evolve if by adding alloying elements such as Cr, Mo, Va on one hand Ni and Cr on the other hand, one would modify the composition of the stable carbide phase at the temperature at which the test is carried out.(*)

We will now tell the reader of this report, how we have dissociated the variations of the physical characteristics, which are on one hand due to the structural modifications consequent upon the metal staying in an enclosure, in which a high temperature reigns (ageing) and on the other hand, due to the particular action of the hydrogen under pressure.

To this purpose, we have taken from round bars forged to a diameter equal to 100 mm, a bomb, of which a drawing is shown in the figure 6 . A blind hole, which communicates with the compressor is made in said bomb. We have assumed that the metal of the bomb around said blind hole was subjected to the action of the hydrogen under pressure at the temperature, at which the test was carried out, whereas it had simultaneously to withstand the internal stresses, arising from its being subjected to said pressure, which stresses have been calculated.

As regards the metal of which the external zones of the bomb is made, and owing to its dimensions, we can say its internal stresses are negligible. On the other hand, as none of the bombs did not leak when being tested, we may assume that the alterations of the metal in these zones are only due to the action of the temperature.

(*) The experimental device, made use of to this purpose is shown on figures 6 and 7. It is easily understood and needs no further comments.

Let us now say that the tests have been carried out up to temperatures, equal to 550, 600, 650 and 700°C, their duration amounting to 1.000 hours.

The results of the Charpy V notch test have been used for jugding the alterations of the metal tested, said notched bar being broken at the ambient temperature. The metal prism used for making said notched bar has been taken from the bomb in a direction parallel to the axis of the latter.

With a view to elucidating the results obtained, we have concurrently studied the problem by making use of metallographic methods, which induced us:

1) to determine the nominal composition of the carbide phase before and after carrying out the test and to study the nature of this phase by diffracting X-rays through the latter. We have thus been induced to develop microanalytic methods for quantitative analysis by having recourse to the standard methods of the chemistry as well as by those of the X-rays fluorescence spectrography.

2) to study by having recourse to the methods of the optical and electronic micrography, the structural modifications to which the evolution of the physical properties of the metal studied may be attributed.

3) to determine the quantity of hydrogen, absorbed by the metal.

x x
x

2. Experimental results (5)

The different steel grades studied have a composition expressed in percentages, which is shown in following table III.

They have been arranged in the order of their increasing chrome-contents and for the same chrome-content, in the order of the increasing percentages of alloying elements.

We have thus investigated all the Cr-variations from 2.25 % Cr to 18 % Cr, the following intermediate percentages of 5, 7, 9 and 14 % being included and not omitting the austenitic steel grades of the types 304 and 321 AISI.

Table III

Composition of the studied steels.

Grades	C	Mn	Si	Ni	Cr	Mo	Va	Other components
I	0.13	0.87	0.36	n.d.	2.25	1.04		
II	0.10	0.25	0.34	0.75	4.76	0.84		
III	0.13	0.55	0.28	0.23	5.74	-		
IV	0.15	0.46	0.31	0.20	5.94	0.52		
V	0.23	0.34	0.40	0.18	4.98	0.70		
VI	0.20	0.51	0.42	0.18	5.46	0.61	0.34	
VII	0.145	0.63	0.32	0.12	5.19	1.10		
VIII	0.17	0.53	0.66	0.36	7.62	1.17		
IX	0.15	0.66	0.34	0.18	9.04	1.10		
X	0.15	0.70	0.48	0.15	9.12	2.08	0.55	Cb 0.39 Cb 1.78
XI	0.12	0.52	0.36	0.74	12.28			
XII	0.12	-	0.84	0.72	13.90			
XIII	0.07	1.80	0.48	9.40	17.73			
XIV	0.06	1.75	0.54	11.00	17.58			Ti 040

3. Discussion of the results.

The analysis of the results obtained, is facilitated by the following diagrams showing how the resiliency varies with the temperature as regards each type of metal analysed. In this respect, each diagram shows separated curves, one relating to the central part of the bomb namely to a part of the latter, where the metal is subjected to the action of the hydrogen and to stresses, induced by putting the metal under pressure, whereas the other one relates to a metal of the external zone, where the thermal stresses are practically the only ones, which may alter the characteristics of the metal. Consequently the distance between both curves can be considered as measuring the action of the hydrogen when this gas is put into contact with a metal subjected to mechanical forces.

A third curve shows how the resiliency of a separated test-piece varies when said piece has been put into the corresponding bomb. This curve compared to the first one, shows how the internal stresses influence the behaviour of the metal in the presence of hydrogen, at a high pressure.

These results will now be discussed by first dividing the different steel grades into three classes:

A. First class - steel with a Cr-content reaching 2.25 %.
B. Second class - steel with a Cr-content ranging from 4 % to 9 %, with variable Mo- and eventually variable Va-content.
C. Third class - steel with a Cr-content exceeding 12 % and austenitic alloys.

A. Alloys with a 2.25 % Cr-content and a 1 % Mo-content.

The carbide phase, rich in Fe (iron) reacts upon the hydrogen at a temperature exceeding 550°C so that the metal loses at this temperature all the properties of the metallic state.

B. Alloys with a Cr-content ranging from 5 % to 9 % and with variable Mo-contents.

a) Let us now consider the steel with a 5 % Cr-content Mo being not present in said steel. Although the carbide phase of this steel is richer in Cr and although no lack of cohesion is revealed by the optical microscope at the joints of the grains, the steel becomes brittle at a temperature exceeding 550°C.

The presence of internal stresses speeds up the process of the steel destruction, which depends upon the structural state of this metal and the presence of ferrite, which makes the steel the more brittle as this ferrite has become considerably less richer in Cr. (A simple calculation shows that if the carbon is entirely precipitated in the form of carbides, there is practically no more Cr left in the base metal after slow cooling and subsequent tempering).

It seems that the fragility of this type of steel comes from the hydrogen atoms being inserted in the iron lattice. The metal becomes ductiles again when it is heat-treated.

b) In the presence of Mo, the Cr-content of the carbide decreases; generally a new type of carbide, rich in Mo, makes its appearance. The Cr-content of the ferrite increases and the fragility develops more slowly.

In fact, we have observed that:

1) as regards the steel with 6 % and 0,5 % Mo-content, the Cr- and Mo-contents are respectively equal to 40 % and to 8 to 9 % (atomic state) in the carbide phase after a normalizing and tempering treatment; these contents amount respectively to 40 and 6 % after slowly cooling said steel and after annealing it

at a temperature of 725°C.

After the first heat-treatment, the separation of the carbide α phase is not completed, because a maximum quantity of Cr is kept dissolved in the base metal. This separation is however complets after the second heat-treatment.

After a normalizing and tempering treatment, the fragility appears at temperatures exceeding 600°C without reaching a dangerous level if we take into consideration that the test is carried out within a relatively short time.

On the other hand, after a completa annealing treatment, the ductility disappears at a temperature exceeding 550°C, whereas the micrographs do not reveal any intercrystalline disintegration.

2) As regards steel containing following percentages of alloying additions, namely 5, 4 % Cr, 0,6 Mo and 0,35 % Va the greater part of Cr, owing to the carbide phase containing a high percentage of Va, remains dissolved in the ferrite, which consequently has not been made brittle by the hydrogen. This steel grade has remained remarkably stable, both structurally and physicochemically.

3) As regards steel containing following percentages of alloying additions namely 5 % Cr, 1 % Mo its staying in an enclosure at the temperatures at which the tests have been carried out, has caused a carbide phase, rich in Mo, to be separated, whereas the Cr-content of the ferritic metal base has not decreased so that the alloy has remained stable in the presence of H_2 even at temperatures exceeding 600°C.

As signs of fragility have been revealed by carrying out cross resilience tests at a temperature of 650°C, it is no recommandable to use this steel grade at this temperature.

The same conclusions apply to the steel containing 7 % Cr and 1 % Mo. This steel grade, previously heat-treated, had engendered a carbide phase, less rich in Mo (5 - 6 % in the atomic state) so that the metal was in a more stable state, as it contained a ferrite, less alloyed with Cr. The cross resilience which brings out the fragility of the metal, shows that said metal at the temperature of 650°C is less stable in the presence of H_2.

4) These conclusions also apply to steel grades with 9 % Cr-content, which after subjecting them to an air-hardening and tempering treatment show no evident signs of fragility at temperature of 600°C. These steel grades after heat-treating them this way engender a carbide, rich in Cr but after annealing them and entirely separating the carbide phase show some fragility at the temperature of 600°C and a tendency of becoming brittle at the temperature of 650°C.

C. Alloys containing more than 12 % Cr and austenitic Ni-Cr alloys.

Such alloys are entirely stable as well from the physical point of view as from the physicochemical one. Temperatures amounting to 700°C can easily be reached provided the apparatuses are dimensioned so that they do not creep, when being put into use.

4. Conclusions.

a) Between the temperatures of 550 and 600°C, steel grades containing 5 to 9 % Cr and some alloying metals are physicochemically stable in the presence of hydrogen under pressure provided the chemical composition and the heat treatment have been adequate so that the ferrite contains a sufficiently high Cr-percentage.

Metallurgists are now interested in alloys containing 5 % Cr-Mo-Va.

b) At temperatures equal to 650°C or exceeding this value, the steel grades with chrome contents equal to 12 % and more are physicochemically stable in the presence of hydrogen.

It may however happen that alloys with a 12 % Cr-content do not mechanically withstand the forces to which they are subjected . This is the reason why we give our preference to the austenitic alloys whether stabilized or not.

Besides, we will note:

1) that the carbides, poor in Cr and Mo, are chemically instable in the presence of hydrogen.
This is reason why steel grades with Cr- and Mo-contents respectively equal to 2,25 % Cr and 1 % Mo are grades in which we take no interest, at least at temperatures in the region of 550°C.
In this case the pressure is a parameter of a secondary importance.

2) A base metal, poor in Cr and in which a carbide phase chemically stable in the presence of H_2 is scattered, becomes brittle when H_2 is inserted in the lattice of the ferritic base metal. The metal becomes ductile again by being adequately heat-treated.
The presence of internal stresses apparently catalyses the cation of hydrogen.

3) A base metal sufficiently rich in Cr and in which a carbide phase, stable in the presence of H_2 is perfectly corrosion-resisting.

4) The austenitic Ni-Cr alloys, although they absorb important volumes of molecular hydrogen do not lose their ductility.

By closing this technical report, we draw the reader's attention to the fact, that in said report we have only corroborated by bringing them out and elucidating certain points, the results published by several authors particularly Prof. B. Dodge.

x x
x

The corrosion of different steel grades by dry hydrogen sulphide with a water percentage equal to 5 % is the subject of a research which is now in progress. The methods used to this purpose are the same as those described above.

Before carrying out our tests, we had to develop a method for compressing the hydrogen sulphide up to a pressure, equal to 1 500 kg/cm2. The execution of said tests started in 1964 and different steel grades were tested. The experimental data collected are however insufficient, as regards their number, so that we are not in a position to publish conclusive results.

III. RESEARCH ON THERMODYNAMIC PROPERTIES OF GASES.

During several years, we have endeavour to study thermodynamic properties of gases used in the industry, and more specially the compressibility, the specific heat and the viscosity of several gases and mixtures.

This work is more a fundamental one, so that in this paper just some aspects relating to industry will be discussed.

The velocity of chemical reactions, their reactions rates and their velocity equilibrium constants can be calculated only by means of accurate thermodynamic data.

Such data are almost completely missing, when reactions occur in a gaseous phase, at pressures exceeding 1000 atmospheres.

Therefore, the "Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture" (I.R.S.I.A.) granted the "Institut Belge des Hautes Pressions", generous subsidies for erecting a laboratory for the study of experimental thermodynamics, under high pressures.

The equation of state of gases is one of the most important notion to be defined in the thermodynamics of high pressures. In fact, the influence of the pressure on the chemical equilibrium of the reaction studied, can be deduced by means of said thermodynamic data, resulting from the study of either pure constituents or mixtures of them, when the equilibrium is reached. Particularly, the gases equation of state must be known for correctly applying several methods of calculations, based on the knowledge of the specific heat of gases, under normal conditions and the variations of the entropies and enthalpies of the same gases, in dependence with their pressures.

The measurement of such quantities takes a long time and moreover, is difficult and expensive. Apparently, it cannot only be made for reactions already used in the industry and of which it is desirable to improve the efficiency, by better knowledge about their equilibrium constants under high pressures.

As examples of such cases, one can mention the ammonia synthesis and numerous reactions, based on methane. This justifies the selection of the gases, we have studied, namely, the stoichometric mixture $N_2 + 3H_2$, and the methane which was the subject of my paper on the Third Symposium on Thermophysical Properties (Purdue University, 22-25th March 1965).

The determination of these quantities raises however technical problems, which are so difficult to solve, that very few laboratories indeed are in a position, to make such measurements. The Belgian Institute for High Pressures made a special study of this field and determines the gase equations of state using a method, derived from Amagat's one. A method for establishing the equations of state has been carefully studied and after receiving successive amendments, has been definitively adopted. Some details are given about the techniques applied to this purpose in the mentionned paper (6).

The experimental results, seem particularly interesting, because inflexion or inversion points are observed in the curves showing how the compressibility, the fugacity coefficient and the fugacity itself vary with the pressure, such observation being made, when the pressure reaches defined value in the region of 2000 atmospheres (Figure 9 gives the fugacity coefficient of methane up to 3000 atmospheres).

IV. ACKNOWLEDGMENT.

All the researches of the "Institut Belge des Hautes Pressions" were made possible by generous financial support from the "Institut pour l'Encouragement de la Recherche Scientifique dans l' Industrie et l'Agriculture "I.R.S.I.A.", and the Belgian Industry: therefore we have pleasure in conveying to the Industry and this Institute our most sincere gratitude.

I express also our sincere thanks to all my research and technical fellows who were associated with this work for numerous years.

June 1965.

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(1) L. Deffet, Les travaux de recherche sous pressions élevées, Compte-rendu du XXXI Congrès International de Chimie Industrielle, Liège 1959, 1, 251.

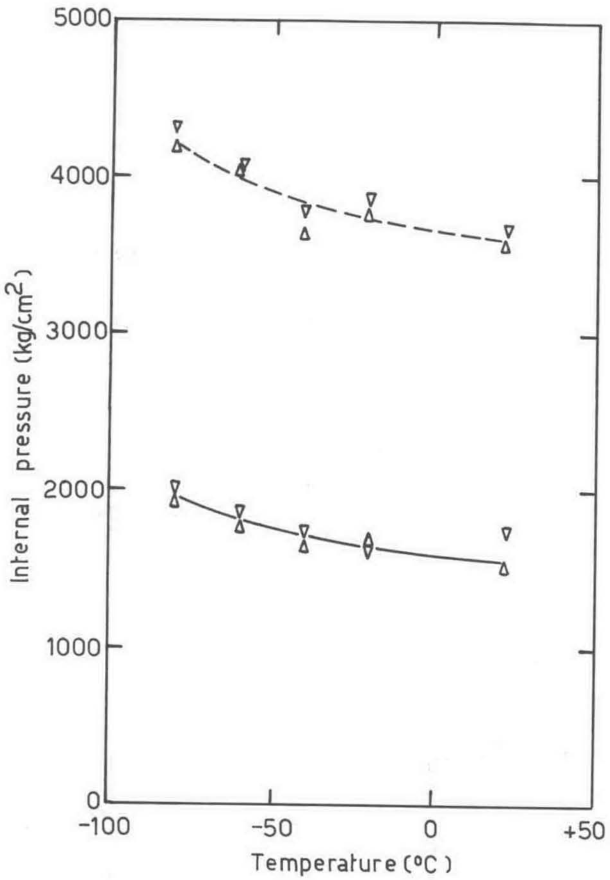
(2) L. Deffet et Lialine, L'influence de l'épaisseur des tubes sur leur comportement sous pression, Acta Technica Belgica 1959, 5, 1.

(3) According to a note: Recherches sur les cylindres à parois épaisses et sur les éprouvettes tubulaires by J. Gouzou, of the "Centre National de Recherches Métallurgiques", Septembre 1964.

(4) L. Deffet, L'apport des hautes pressions à l'industrie chimique, Industrie Chimique Belge, 1962, 27, 335.
L'influence des hautes pressions en chimieet en thermodynamique, Thermotecnica (Milano) 1963, 17, 646.
Appareillage et méthodes de recherche en chimie, sous hautes pressions, Chimia (Aarau), 1964, 18, 89.

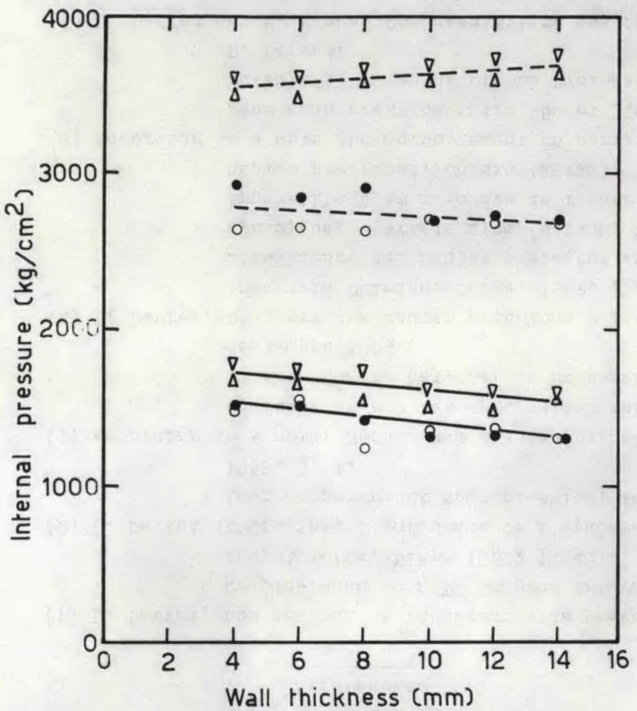
(5) According to a note "Le comportement de certains aciers à l'hydrogène sous pression entre 550 et 700°C, by R. Berger, Scientific Director of the "Usines E. Henricot" and L. Deffet.

(6) L. Deffet and F. Ficks, Compressibility and fugacity of methane up to 3000 atmospheres and 150°C. Advances in Thermophysical Properties at Extreme temperatures and Pressures, Editor S. Gratch. The American Society of Mechanical Engineers, New York, 1965, p. 107.



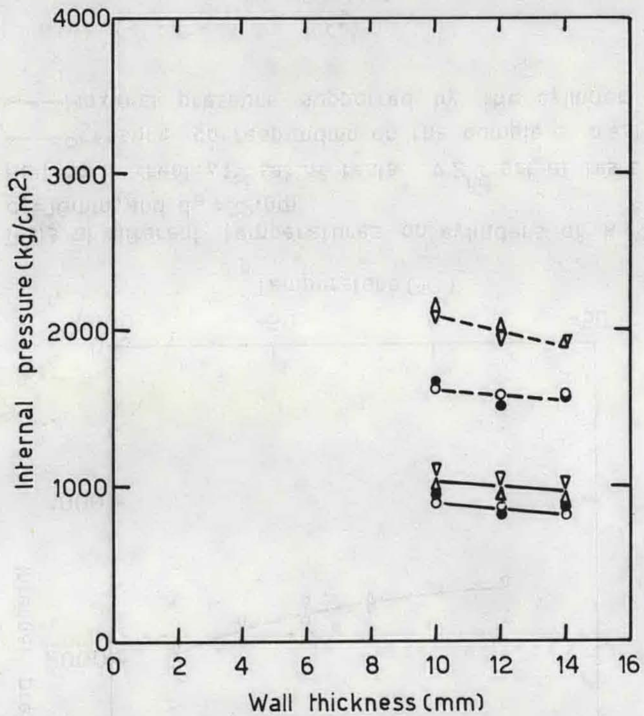
Tests at different temperatures on cylinders of k = 2 ratio, with d_i = 16mm, and d_e = 32mm
Half-hard steel: Δ 1st set of tests ∇ 2nd set of tests
—— Pressure corresponding on the complete plasticity.
- - - - Maximal pressure supported by the cylinder before rupture.

Figure 1



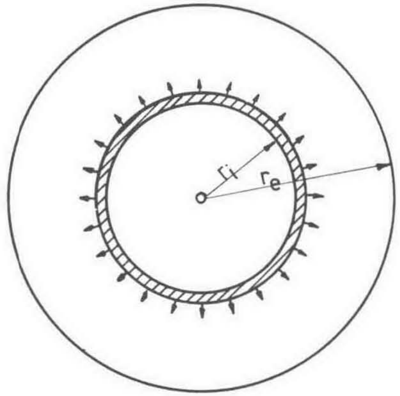
Tests on ambient temperature on cylinders of k=2 ratio
Mild steel: ○ 1st set of tests ● 2nd set of tests
Half-hard steel: △ 1st set of tests ▽ 2nd set of tests
——Pressure corresponding on the complete plasticity.
- - -Maximal pressure supported by the cylinder before rupture.

Figure 2



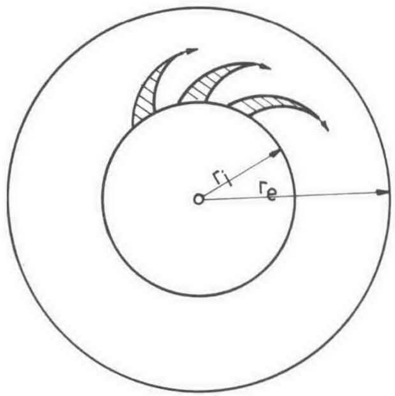
Tests on ambient temperature on cylinders of k=1.5 ratio
Mild steel: ○ 1st set of tests ● 2nd set of tests
Half-hard steel: △ 1st set of tests ▽ 2nd set of tests
——Pressure corresponding on the complete plasticity.
- - -Maximal pressure supported by the cylinder before rupture.

Figure 3



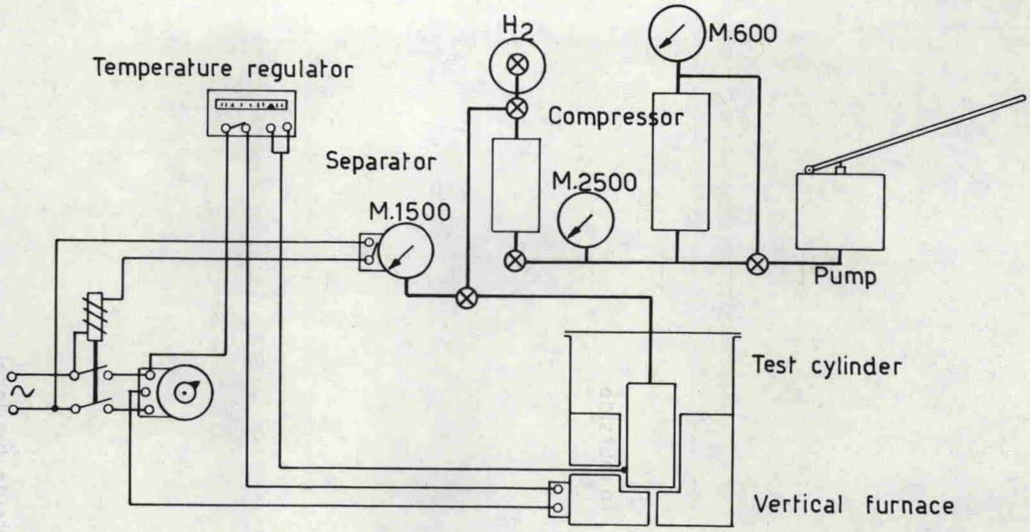
Plastic deformation progression from inside to outside by concentrical layers.

Figure 4



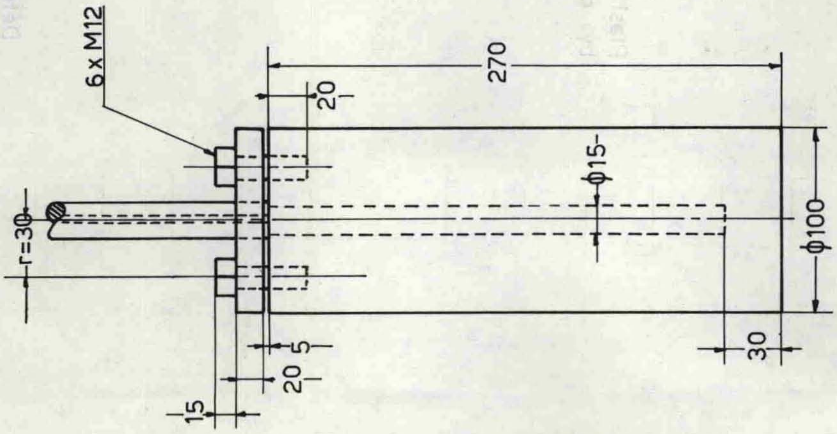
Deformation progression from inside to outside by local plastic deformations.

Figure 5



Experimental device

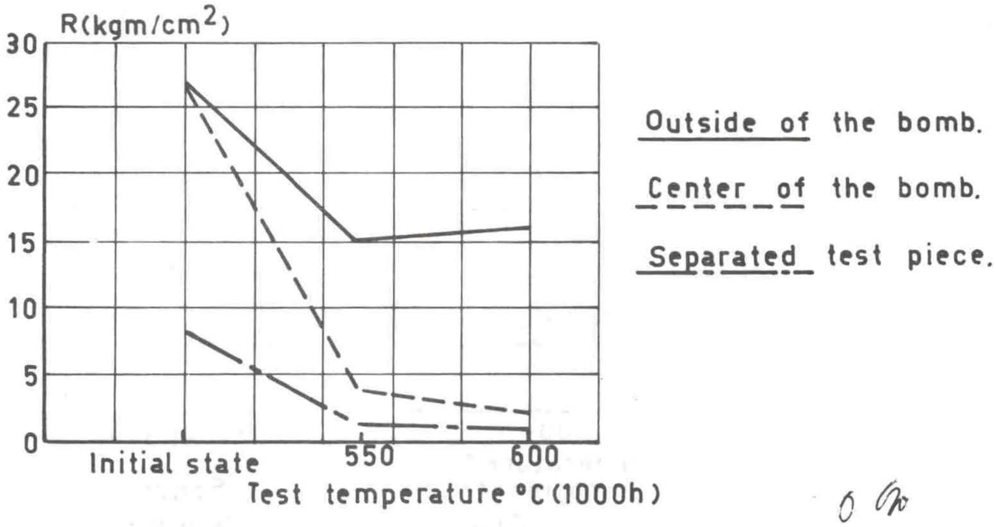
Figure 7



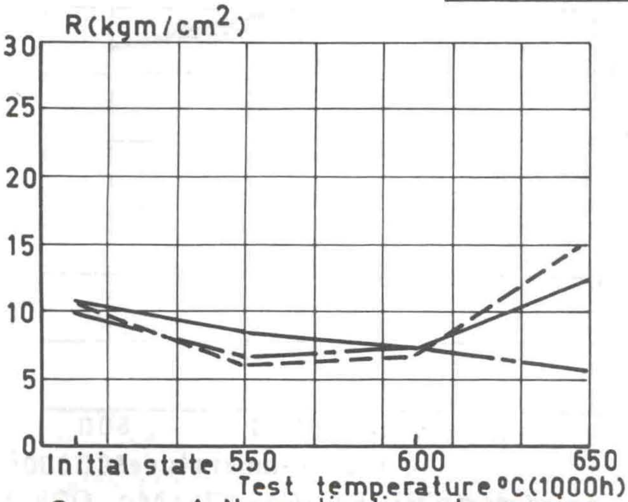
Test cylinder

Figure 6

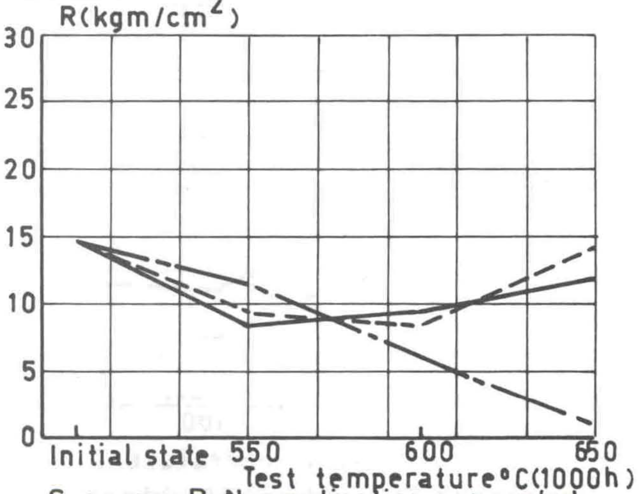
Figure 8



Grade I. 2.25% Cr. 1% Mo.

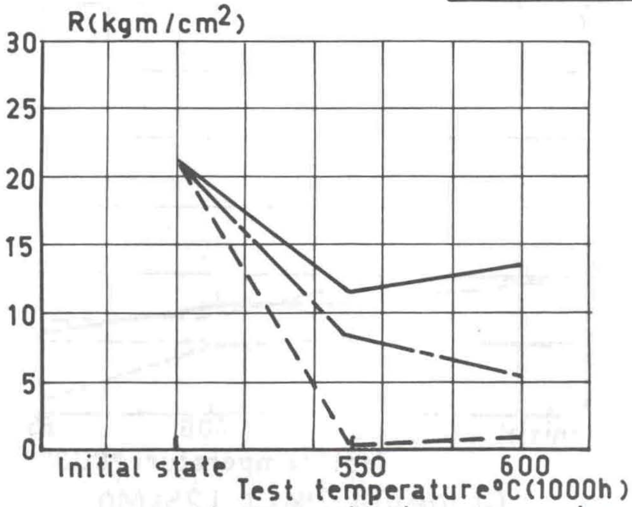


Sequence A. Normalisation + tempering.

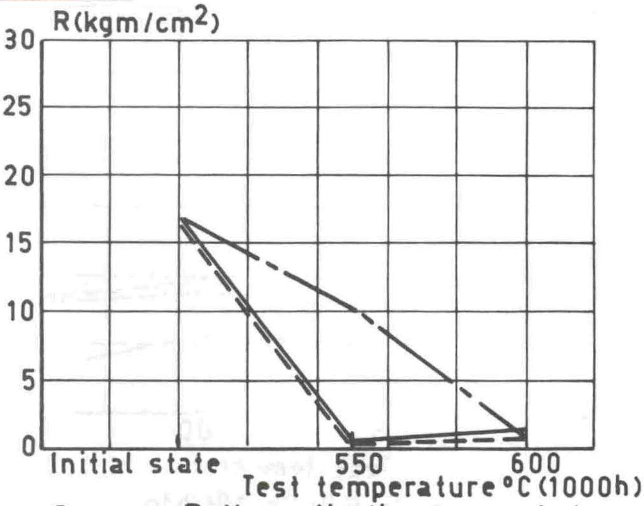


Sequence B. Normalisation + annealed.

Grade II. 4% Cr. 1% Mo.

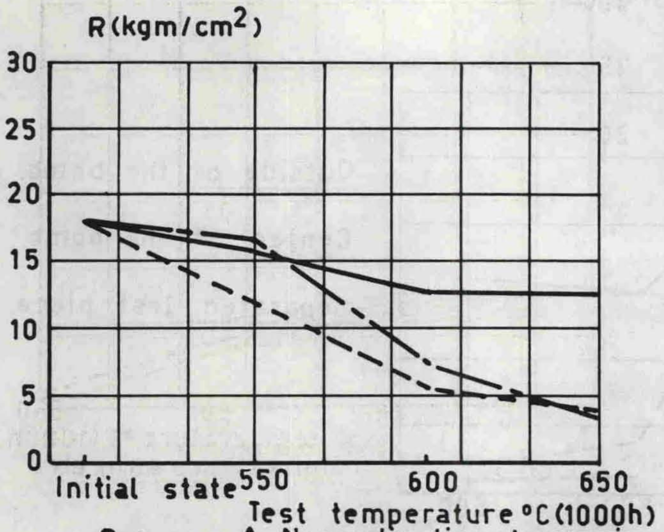


Sequence A. Normalisation + tempering.

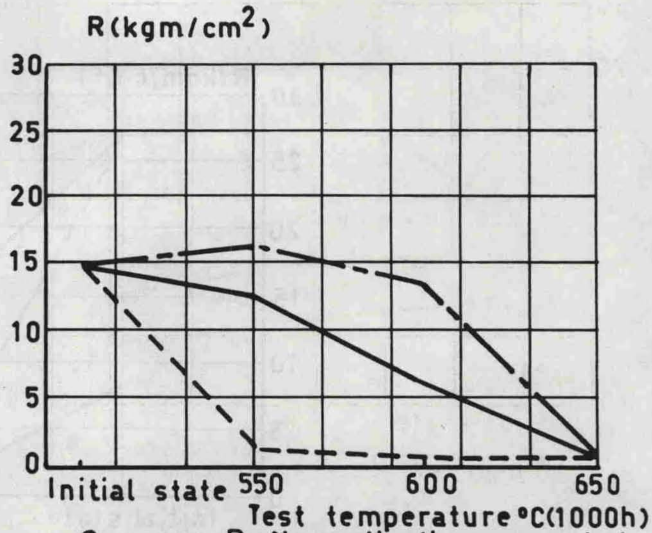


Sequence B. Normalisation + annealed.

Grade III. 5% Cr.

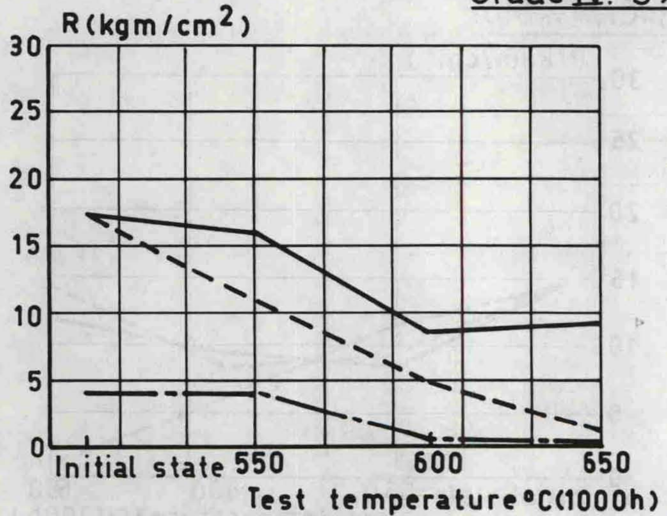


Sequence A Normalisation+tempering.

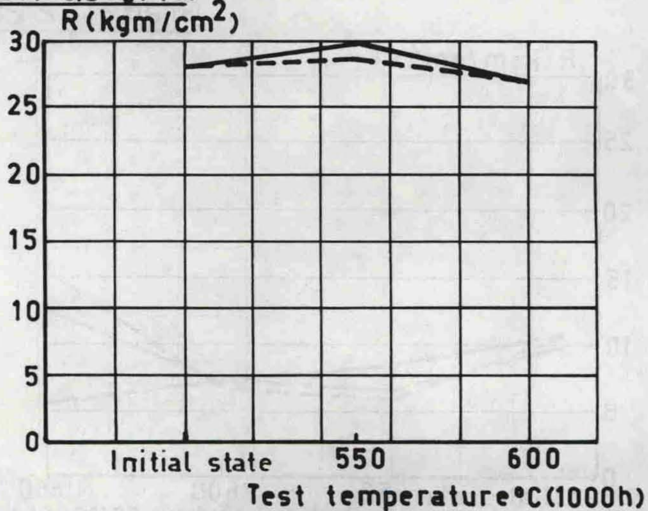


Sequence B Normalisation+annealed.

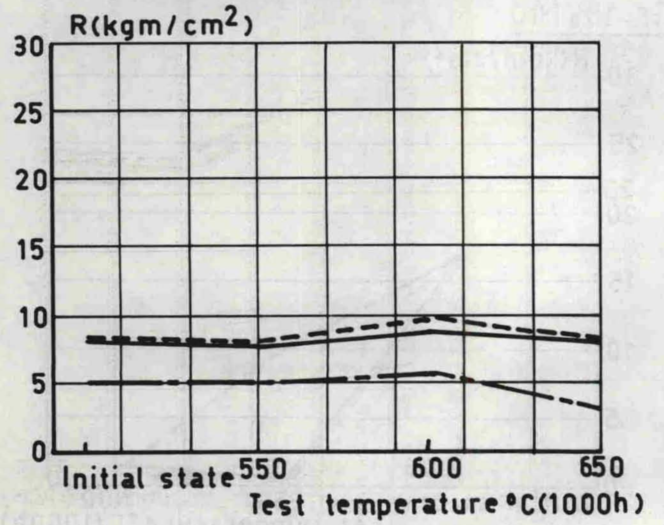
Grade IV. 5%Cr. 0.5%Mo.



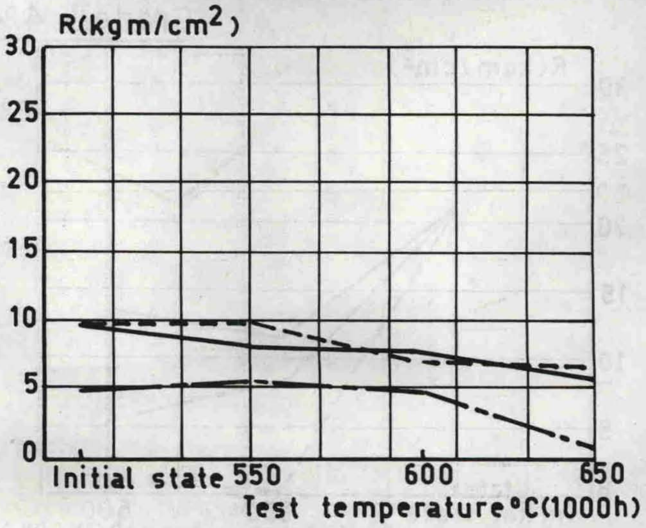
Grade V. 5% Cr. 0.7% Mo.



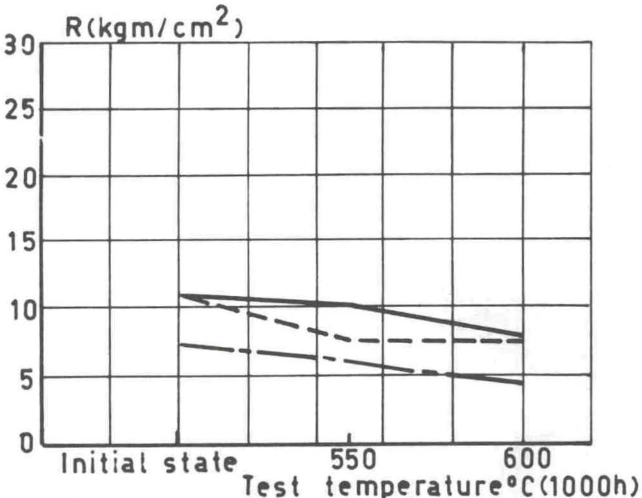
Grade VI. 5% Cr. 0.7% Mo. 0.3% Va.



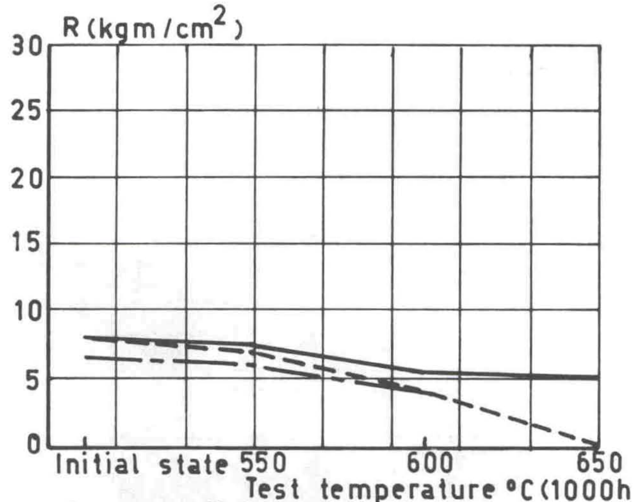
Grade VII. 5% Cr. 1% Mo.



Grade VIII. 7% Cr. 1.2% Mo.

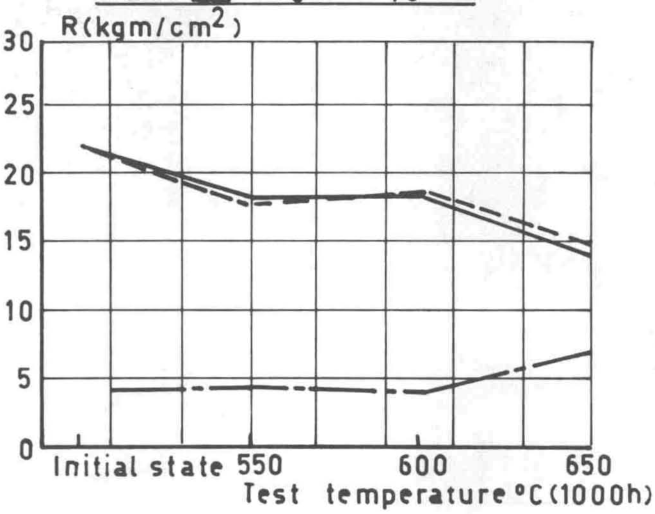


Sequence A. Normalisation + tempering.

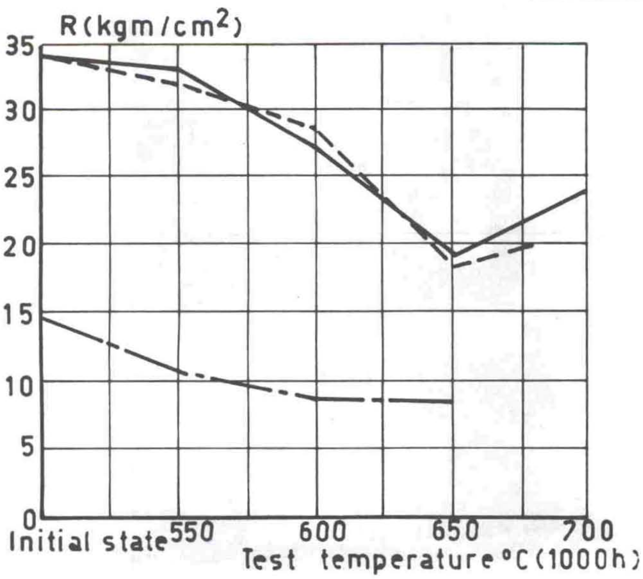


Sequence B. Normalisation + annealed.

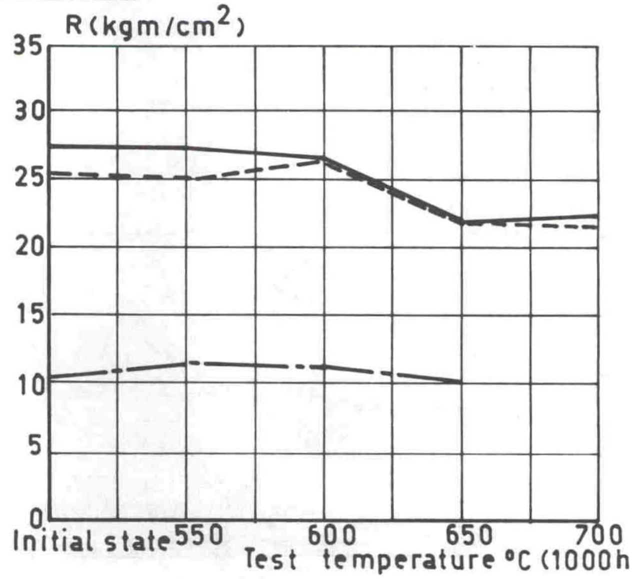
Grade IX. 9% Cr. 1% Mo.



Grade XI. 12% Cr.



Grade XIII. 304 AISI.



Grade XIV 321 AISI.

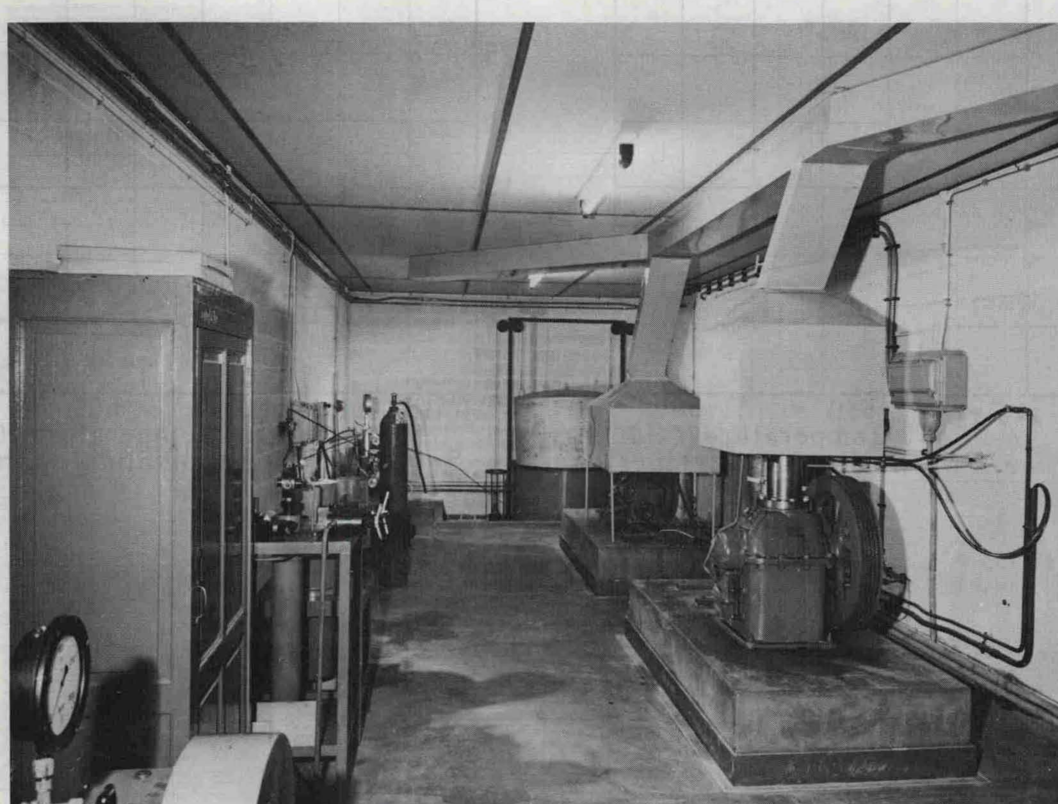


Figure 1.


Figure 2.