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Strength of Glass (A Review)

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After defining the term *glass*, brief consideration is given to the theories of glass structure which have been propounded. That glass, in practice, is very much weaker than its theoretical strength predicts is established, and the prime factor for this is shown to be the surface condition of the glass. Surface defects which are accentuated by heat treatment or other processes are considered, and the effects of the structural state, loading, and water and other liquids are dealt with. Methods of measuring the strength of glass are discussed and techniques of strength reinforcement, particularly in respect of producing a flaw-free surface and protecting it against subsequent damage, in the light of current knowledge are indicated. Many possible techniques for achieving strengthening have been postulated in the literature and some of these have now been commercially applied. Particularly, thermal and chemical toughening processes – the latter including ion-diffusion techniques recently developed – are reviewed. Where possible, references to the original papers and patents are provided. The references given, whilst not comprehensive, will permit a wider study of the subject.

1. Introduction

The term *glass*, as understood by glass technologists, embraces many substances, but generally refers to a material which is transparent and, at room temperature, brittle. A prerequisite of any discussion on the strength of glass and ways in which it can be strengthened is a definition of *glass*. When a liquid cools to the point at which it is solid, i.e. possesses a viscosity greater than $10^{14.5}$ poises (according to Condon [1]), it becomes, if no crystallisation occurs, a glass, and has no long-range order or three-dimensional periodicity. As the majority of experimental work has been concerned with silicate glasses, it is with these glasses mainly that we shall be concerned in this review.

In the last few decades, many hundreds of papers have been published relating to the strength of glass, and it is obviously impossible, in a short review, to do justice to all the workers and papers in this field. However, because many of the more recent publications are concerned with the strengthening of glass, it is desirable that, although detailed discussion of glass structure cannot be entertained, some indication of the contributions on this subject is given.

Randall *et al* [2], from X-ray examinations on vitreous materials, concluded that glasses were aggregates of extremely small crystals or crystallites. Earlier, Lebedev [3] had postulated the crystallite theory, but this theory and a later one, the "Continuous Random Network" theory, whose foundations were laid by the work of Zachariasen [4], and Warren *et al* [5], were both criticised by Valenkov and Porai-Koshits [6]. These workers and others, such as Peyches [7], Zarzychki and Mezard [8], Garino-Canina [9], Stevels [10], etc., have generally postulated models which include some degree of order in units which are themselves within a matrix of low order. Ion location within the structure profoundly affects the physical properties and, under some circumstances, the strength of glass.

2. Theoretical Strength of Glass

In attempting to derive the theoretical strength of glass, all calculations are, of necessity, only approximate, in that properties of the material involved in the calculations are not sufficiently accurately known. Polanyi [11], Orowan [12], Condon [1], Griffith [13], as well as other workers, have deduced strengths all of the same order: 1×10^3 to 3×10^3 kg/mm^2. Most glasses have moduli of elasticity of approximately 7×10^3 kg/mm^2, and thus it is seen that from theoretical considerations, assuming the validity of Hooke's law to the breaking stress, strains of 20% should be possible. Extensions of this order are never realised, owing to a practical breaking strength considerably lower than the theoretical.

3. Practical Strength of Glass

In practice, strengths of bulk glass in excess of 5 kg/mm^2 are seldom realised; if they are it is because of additional process treatment. Fibre strengths, because of the near-perfect surfaces of these materials, can be much higher. The predominance of the effect of the glass surface on strength is now widely appreciated, but, as will be indicated later, other factors do play their part. The concept of the state of the surface determining the practical strength is not a new one, and it was probably first realised or indicated by Littleton [14] and referred to by Preston [15] in a statement: "We do not measure the strength of glass, we measure the weakness of the surface."

Griffith postulated that glass contained numerous microscopic flaws and cracks, and that surface cracks were more potent than internal ones. Although many workers have attempted to explain the low strength of glass in terms of Griffith's concept, a completely satisfactory solution is still not evident. It is not possible in this short review to consider all the factors affecting the strength of glass, if, in fact, they are all known, and only those whose effect has been demonstrated will be considered.

3.1. Effect of Surface Damage

It is well known that sheet glass will, under load, withstand a higher pressure than plate glass [16], and, although there are slight compositional differences, the prime difference is the state of the surface. Plate glass is ground and polished, whereas sheet glass is drawn from the melt and fire-finished. Fire-finishing or fire-polishing is an established method of restrengthening glass weakened by grinding, and as much as a four-fold increase in strength by fire-polishing over mechanical polishing is possible. Traditionally, also, glass etched under controlled conditions in HF solutions can be greatly strengthened, and this has been demonstrated by, among others, Müller [17], Proctor [18], and Symmers *et al* [19]. On glass rods of soda-lime-silica composition, strengths in excess of 300 kg/mm^2 have been reported, and this figure has been closely approached by strength tests on freshly blown glass. These strengths closely approach the strength of pristine or virgin glass, and although earlier workers, particularly Griffith [13] and Anderegg [20], concluded that the tensile breaking strength of glass, tested in the form of fibres, was closely dependent upon diameter, later work, notably by Otto [21] and Thomas [22], has shown that no such correlation exists. However, conditions of forming of the fibres can affect the strength. It is believed that many of the earlier workers inadvertently created surface damage of the fibres before test, either by mechanical abrasion on a winding drum, or by chemical damage by the effect of atmospheric contamination or moisture in the period between manufacture of the fibres and test. Whereas the strength results of early workers were subject to coefficients of variation of 30% or higher, later work of Thomas [22] indicated that, by controlled experimentation and testing conditions, coefficients of variation of the order of 1% were possible.

3.2. Deduction and Origin of Surface Damage

Flaws in the surface of glass of a size below 100 Å in width cannot be revealed by conventional optical aids, and, although flaws of 10 Å width could produce substantial stress raisers with the attendant loss in strength, electron microscopy has not positively identified such flaws. Indirect techniques by sodium-vapour treatment, carried out by Andrade and Tsien [23], Gordon *et al* [24], Argon [25], and Nakayama [26], are now believed to have demonstrated expansion changes and defects in the surface brought about by the sodium-vapour treatment. Ernsberger [27], by a very elegant technique of ion exchange by lithium salts, has concluded that, although the defects revealed by the previous sodium treatments were caused by expansion differences, the real origin of them was in Griffith flaws. Levengood [28] has shown, by a sodium fluoride reaction on a glass surface, that small defects react differently to larger cracks, and that the strength of the article could be correlated with the number and orientation of the flaws.

It may be concluded, therefore, that, although many surface defects can be detected by optical or electron microscopy and revealed by ion exchange techniques, the fundamental cracks, flaws, or defects, which could explain the wide range of strengths generally obtained, have never been revealed.

The presence of gross defects on the surface of glass is a result of mechanical contact and damage. Although such damage drastically reduces the strength of virgin glass, some flaws must still be assumed to be present in virgin glass, which reduce its strength to about 300 kg/mm^2. These flaws may be surface flaws of depths of the order of 100 Å, or internal flaws or bubbles which have hitherto escaped identification. Brearley and Holloway [29], from a detailed examination of the broken surfaces of tensile testpieces, conclusively showed that in many cases fracture was due to surface inclusions and further postulated that dust or contaminating particles settling on the surface during the drawing process could introduce surface defects. Contamination by atmospheric attack which might yield microcrystalline particles could also conceivably provide the origin of some surface flaws. To extend this discussion to glasses other than soda-lime-silica glasses does complicate the question, but Cornelissen and Zijlstra [30] have shown that composition exhibits only a limited effect upon strength if the glass is in the pristine or virgin state. Speculation as to whether chemical attack is responsible for the formation of small flaws up to the order of 100 Å is obviously reasonable.

3.3. Effect of Structural State

The apparent dependence of strength upon specimen size led many workers to explore in greater detail any differences in structure which might correlate with strength measurements. Experiments by Griffith [13], Smekal [31], Anderegg [20], and Murgatroyd [32] deserve special mention. Smekal argued that the stresses arising in the fast cooling of fibres would be contributory to the apparent higher strength of fibres. Anderson [33], however, showed that the fibres could not be heat-strengthened or toughened owing to the cooling rate. Bartenov and Bovkeumenko [34] suggested that the whole fibre structure had become orientated. Powell and Preston [35], on the other hand, indicated that orientation, if it plays a part, cannot be the only explanation of the size effect on strength. Murgatroyd suggested a "viscous pocket" inside an elastic matrix. Anderegg [20] and Kontorova [36] believed that bubbles in more massive glass might be the weakening effect, which, if elongated to thin air-lines when glass was drawn into fibres, would not act as strength weakeners. This latter postulate has been confirmed by Cornelissen [30], who showed that elongated air-lines do not weaken virgin glass. Although the work of Otto [21] showed an independence of strength on diameter provided certain manufacturing conditions obtained, he did conclude that fibres drawn at a low temperature, which were generally thicker fibres, could be weaker as a result of this lower drawing temperature. This is in opposition to the conclusion of Thomas [22]. It may be concluded that the experimental evidence now available indicates that size effects appear to be slight, and virgin strengths in bulk glass can be obtained which closely approach recorded strengths for fibres, and hence thermal history and orientation can have only a slight influence.

3.4. Effect of Temperature

The effect of heating both rods and fibres of virgin or HF-strengthened glass has been investigated by Thomas [22], Otto [21], Brearley and Holloway [29], and Ward *et al* [37], and there is no doubt that heating in a normal atmosphere to temperatures as low as 100° C does weaken such samples. In many cases, the experiments are not conclusive, in that any absorbed moisture which might have a healing effect could, on removal, cause weakening. Surface damage resulting from the heating must be contributory at higher heating temperatures, and it has been shown by Sakka [38] and Zijlstra [39] that this surface damage can be removed by a subsequent HF etch. Although Brearley and Holloway believe that the heat-weakening effect is due to the bonding of contaminating particles to the glass surface, they nevertheless acknowledge that water immersion does yield a recovery in strength. Further, recovery of strength in air could be due to the presence of moisture in the air. This view is endorsed by the fact that in dry nitrogen the recovery of strength is inhibited. Ward *et al* have also reported [37] that HF-etched samples, heat-treated at 350° C and consequently weakened, fully recover their strength on water immersion.

3.5. Effect of Moisture and Other Liquids

Although, as has been previously indicated, water can produce a strengthening in glass, it can also, under some conditions, have the opposite effect.

Radd and Oertle [40] believed water effected a chemical solution, because, after drying out specimens which had been treated in aqueous solutions, strength reversions did not occur. Culf [41] investigated the effect of water on glass under stress, and for specimens under tension the effect was most pronounced. The removal of moisture, she concluded, yielded an increase in strength. Stockdale *et al* [42], whilst suggesting in one paper that the reduction in glass strength when specimens were broken under water was due to capillary action with a resultant high pressure within a flaw, provided an alternative postulate: that reaction products opened a flaw and increased the apex stress. The effect of various organic liquids has been investigated by Moorthy and Tooley [43], and Thomas [22]. Moorthy and Tooley found that, for a given loading time, glass was 36% stronger under alcohol than under water. Thomas, after exploring the effects of various organic solvents, including acetone, carbon tetrachloride, and toluene, concluded that the solvents used had little weakening effect on glass fibres. Mould [44] has made a comprehensive study of liquid and temperature effects – although mechanically damaged glass could be significantly strengthened by water and by acidic or basic solutions, methanol had little effect. He suggested as a result of his experiments that the increase in strength revealed by Moorthy and Tooley [43] could not be attributable to flaw repair. The work of Watanabe *et al* [45], in investigating the ageing effect of various soda glasses, showed the importance of the sodium oxide content in liquid reactions. Moorthy *et al* [46] also investigated different glasses including lead and borosilicate glasses. Glasses which might be expected to possess the more defective surface eventually showed the greatest strength gain from water immersion.

3.6. Effect of Loading

Many experimenters have in the past investigated apparent fatigue effects, both static and dynamic, in glass, and in the main they have led to the general conclusion that slow rates of loading yield lower strengths. Investigators, for example Borchard [47], McCormick [48], and Holland and Turner [49], concluded that the strength decreased to a limiting value. Baker and Preston [50] found that increasing loading times from milliseconds to hours decreased the strength by some 40%. The effect was more pronounced with wet glass, and zero effect was found for glass baked out *in vacuo* and tested *in vacuo*. These findings were confirmed by later work of Gurney and Pearson [51], who found further no fatigue in dry air or air from which the carbon dioxide had been removed. Recently, extensive studies of fatigue in glass have been made. Little or no fatigue has been found at very low temperatures, and Charles [52] showed that corrosion by water vapour was associated with flaw-tip stress concentrations. Mould and Southwick [53], in the examination of damaged glass samples tested under water, discovered a universal fatigue curve. The fatigue rate under tension varied exponentially with the original flaw size, and a limiting strength was claimed.

It is possible that strengthening and weakening effects can exist together, and the predominance of one over the other may well depend upon the surface condition and the environmental state.

4. Measurement of Strength

Techniques of mechanical-strength determination are naturally varied and diverse, and, in many instances, are determined by the form of a glass sample. For bottles or containers, exact determinations are seldom available, whereas for rods or fibres, accuracy in strength-measurement techniques is frequently achieved. Tensile, torsion, bend, and pressure testing apparatus are the main forms currently used.

Tensile tests are more difficult to conduct if specimens are immersed in liquid, and great care has to be taken to ensure that the gripping of the ends does not damage and weaken the test area. Thomas [22] and Symmers *et al* [19] are authors who have described tensile testing apparatus. Torsion tests, although only infrequently used, have been valuable in demonstrating anisotropic effects. Otto and Preston [54], and Brearley *et al* [55] have adopted this type of test. Bending tests, either three- or four-point bending, are more universally used, and, although corrections to simple bending formulae are necessary for accurate strength determinations, the techniques are readily adaptable to various test conditions of temperature, time, and atmosphere, etc. Workers who have adopted this form of test technique include Baker and Preston [50], Mould and Southwick [53], Proctor [18], Ward *et al* [37]. Pressure tests frequently used for containers have found general favour in strength determinations on flat glass, valves, and laboratory glassware. Equipment used by both Bowles and Sugarman [16] and Schardin and Kerkhof [56] for flat-plate testing enabled corrections for large-deflection theory to be applied.

5. Strength Reinforcement

As has been illustrated previously, the extremely large differential, between the theoretical strength of glass and the practical limit to which one can safely work, is primarily due to the presence of surface defects which must inevitably set up stress raisers which initiate failure at low tensile stresses. There are two basic approaches in strengthening glass (i.e. the utilisation of a greater proportion of the inherent strength of material): (i) producing a flaw-free surface and protecting it against subsequent damage or defects; or (ii) healing surface defects and at the same time making the surface resistant to abrasion.

5.1. Coating and Thermal Toughening

Although pristine glass, which is fire-polished, is at the moment of solidification in its most defect-free condition, subsequent heat treatments and annealing damage the surface. In the container industry, where greater utilisation of the glass strength would promote the more universal use of lightweight bottles and jars, considerable effort has been expended, in the last decade, in exploring various treatments and coatings which would preserve the pristine surface of glass. Various surface coatings have been applied in the annealing lehrs and, whilst many of them are effective in reducing scuffing (a word traditionally used to describe bruising and abrasion primarily as a result of glass-to-glass contact), the benefits are often not permanent. Sulphuring treatment has been frequently adopted, and Douglas and Isard [57] have shown the process to be an ion substitution, whereby sodium in the skin of a conventional soda-lime-silica glass is replaced by hydrogen in the ionic form. Tober [58] established than an alkali-deficient compressive layer is created by SO_2 treatment with an adjacent layer under tensile stress. A further established process in the container industry is the use of pellets of ammonium sulphate [59], but it is believed that the prime effect of this treatment is one of increased durability and not strengthening. More recently, silicone treatments have been commercially applied, and publications by Bumpstead [60], Moody [61], Loewenstein [62], and others have reported increases in impact strength as a result of such treatments. It is believed, however, by both Riedel [63] and Schonbrünn [64], that the coating established is only a very thin film which will not withstand subsequent washing and cleaning. Moody established that effects comparable to those obtained by the use of silicones could be achieved more economically by the use of SO_2 or polyoxyethylenemonostearate treatments. Current work in both the United States and this country has indicated that highly resistant coatings of either TiO_2 or SnO_2 can be generated as very thin films on pristine glass, and they impart very high resistance to scuffing and provide high impact strengths. Application of these metal oxide films is via metal organic compounds or metal halides, by spraying from a liquid or vapour phase. Patents by duPont [65] and United Glass [66] may be cited in this connexion; Lontz *et al* [67] have indicated the very low concentrations of the oxides required to provide adequate protection.

For other forms of glass, i.e. fibres, Loewenstein [62] refers to chrome-complex treatments and silane treatments as a means of strengthening for subsequent use in reinforced plastics. Van Tetterode [68], working with flat glass, obtained significant protection by the use of silicones after HF etching. Silvestrovich and Boguslavskii [69] strengthened both sheet and plate glass by quenching in baths of chlorosilanes. They obtained strengths some two-and-a-half times that obtained by normal air toughening (a technique universally used for flat glass). The authors attributed the increase in strength to the formation of SiO_2 film on the glass. However, in a subsequent paper by Vitman *et al* [70], the explanation given was that of improved heat transfer and greater quenching, resulting in an increased toughening by immersion in silicone.

The inital explanation might be interpreted as analogous to the formation of a skin of glass in compression, and this idea was first developed by Schott [71]. As early as 1892, Schott produced a "cased" glass, wherein the outer skin of glass has a lower coefficient of thermal expansion than the main glass. This technique produces an outer skin in compression which is more able to withstand tensile stresses which cause fracture. The conventional technique of thermal toughening is well established, and this process has been put to use in windscreens, tumblers, and simple pressed articles. The glass is heated to near its softening point and rapidly quenched on the outside, usually by air, although many other media including grease, tar, oil, and waste gases [72] have been used. This outer quenching, whilst the inner glass remains hot, results, on the subsequent solidification of the inside, in a compressive stress on the outer skin.

5.2. Chemical Toughening

Brekhovskikh [73] has mentioned many methods which could, by altering the physicochemical glass structure, affect the strength of glass. The techniques propounded include: (i) action of nuclear radiation (neutrons, protons, gamma-rays); (ii) introduction of additional ions or ionic groups into the structure of the glass (electro-diffusion); (iii) replacing the ions having larger radii by ones having smaller radii (or vice versa); (iv) introduction, into the glass, of neutral inorganic molecules and/or metals in the atomic state; (v) action of high pressure; (vi) orientation of the structure by external influences; (vii) introduction of organic molecules into inorganic glasses; (viii) formation of inorganic polymers.

Of the above techniques, some have already been explored in detail, whereas others have received little attention so far. Not all will be practical or economic, and the present indications could be that ionic substitution by larger or smaller ions is the most attractive and practical process.

Electron and neutron bombardment was investigated by Mike *et al* [74] and Thomson [75], but these experimenters found little effect on the strength of glasses and fused silica. French patents [76], however, have claimed strengthening of alkali borosilicate glasses by neutron bombardment. The controlled cooling of glasses containing metals in the atomic state may result in crystallite aggregation and thus promote crystallised glass, i.e. glass-ceramics. With these materials, plastic flow at flaw tips can occur, with the consequence that surface damage only leads to fracture at comparatively higher stresses. Processes announced by the Corning Glass Co include both ion-diffusion and controlled-crystallisation processes.

Effective ion-diffusion processes were first described in the literature by Kistler [77], who discussed ionic diffusion, at temperatures primarily below the glass softening point, in both his paper and patent [78]. If, for soda-lime-silica glasses, the glass is heat-treated in a potassium nitrate salt bath at temperatures up to about 450° C, then, because of the diffusion into the glass of the larger potassium ion and the diffusion out of the smaller sodium ion, a compressive surface stress results. Baths of molten salts of silver, thallium, and potassium, all of which have larger ionic radii than sodium (see Koranyi [79] or Glasstone [80]), would be expected to have a strengthening effect. If, on the other hand, lithium salt baths are used, then surface tensile stresses result because of the larger size of the sodium ion over that of lithium. This lithium substitution process at temperatures below the softening point has been used by Ernsberger [27] to demonstrate the existence of latent Griffith cracks. In patents issued to the Corning Glass Works [81] and the Pittsburgh Plate Glass Co [82], claims are made that potassium ion-diffusion processes have, in conjunction with additional treatments, not only increased strengths but yielded improved durability and abrasion resistance. Imperial Chemical Industries [83], in patents granted in 1965, refer to composite processes which strengthen glass surfaces by the simultaneous etching of the surface to remove defects, and to the introduction, by ion exchange, of a compressive stress in the surface which resists further damage. The addition of silver nitrate to the potassium nitrate bath in which the glass is immersed apparently increases the rate of the ionic diffusion process. Slight coloration of the glass to golden yellow is reported in this process, but the further addition of cuprous chloride to the batch prevents the coloration without deleterious effects.

Ward *et al* [37] showed that potassium nitrate treatment by itself, although producing strengthening, was a slow process, and concluded that the thickness of the compressive skin formed was probably insufficient to resist normal abrasion adequately. It has been suggested by Stookey *et al* [84] that a layer of 50 μm was the minimum required depth for adequate abrasion resistance. The work of Acloque [85] and Ward *et al* [37] has also indicated that at any temperature of treatment there exists an optimum time of treatment. There is a rise in strength with increasing length of treatment up to a maximum, with a fall back to the original level. The rate of rise of strength increases with temperature of treatment, and the decay in strength is most probably due to stress relaxation. Most chemically toughened or strengthened glasses are now tested after controlled abrasion, and, whereas it is not unusual for untreated glass to break at stresses of 3 to 4 kg/mm^2, ionic diffusion processes alone can result in glasses which will adequately withstand stresses of 10 times this order.

Corning Glass Works [86] have also patented processes which provide strengthened glass by the formation of β-spodumene or β-eucryptite within the glass matrix. In the case of the β-spodumene process, strengthening of special glasses containing TiO_2 is achieved by substitution of lithium from a molten salt bath for sodium, at a temperature above the strain point. The highest glass strengths were obtained in glasses which did not remain transparent after treatment, primarily owing to the presence of TiO_2. The great strengthening is attributed to the formation of β-spondumene, which has a negative, linear thermal expansion coefficient.

Controlled heat treatment of specially fomulated silicate glasses, with lithia present as the prime alkali, can produce microscopic or submicroscopic crystals of β-eucryptite. Again, β-eucryptite has a lower, linear thermal expansion coefficient than the base glass, and therefore after heat treatment a compressive skin stress is produced. Unlike the lithium bath treatment, no compositional change is claimed between the body of the glass and the skin, only a crystallisation which takes place at or near the glass surface. These glasses can be strengthened further by HF treatment prior to the heat treatment. Glass transparency is retained by these second processes, owing to, it is claimed, the fact that the difference in refractive index of the base glass and of the β-eucryptite crystal is only slight.

6. Conclusions

From theoretical calculations, approximate estimates of the ultimate strength of glass have shown that elongations or extensions of up to 20% should be possible before fracture. In practice, elongations several orders less than this are the best that is usually achieved. It can be shown that in the main the reason for the low practical strength can be attributed to defects of the surface, and, whereas size effects were until recently thought to be of prime importance, it is doubtful whether size plays a very significant part in the realisable strength. In addition to the effect of surface damage on strength, there appears to be some factor attributable to the structural state of the glass, but this effect is probably also only small. Temperature effects are significant, but whether the effect is due to moisture removal, or contamination, or surface damage as a result of crystallisation is still uncertain. Fatigue effects also exist, but these are dependent upon the temperature of the test and also the atmosphere surrounding the sample at test.

The problem of strong glass is primarily one of retaining the inherent strength of virgin glass. In so far as glass articles are inevitably subject to contamination and abrasion in manufacture to some degree, it is frequently necessary to treat the surface by, for example, a HF etch, before further processes to retain the regained strength or to reinforce this strength can be applied. Glass breaks in tension, and strengthening or reinforcing processes are effective if they produce compressive skin layers which, when applied forces are active, prevent damaging tensile stresses at exposed surfaces. For commercial soda-lime-silica glasses and special glasses, ion-diffusion processes, jointly with etching processes, appear to be the most promising in achieving the skin compressive stresses necessary for reinforced glass. In the case of special glasses, complete transparency is often impossible with ultra-high strength glasses, but in some cases significant strengthening can be achieved, retaining at the same time the desired transparency of glass.

In this review, an attempt has been made to consider the various facets of the strength of glass which have received the most attention over the past years. Factors such as the hardness of glass have not been considered, although there is some evidence to show that a correlation may exist between hardness and strength. This review cannot be regarded as comprehensive, but it is hoped that it provides a sufficient introduction to the problems to indicate some of the fields in which clarification is desirable. In that the review in itself is not comprehensive, no attempt has been made to record a full bibliography, but the references given will, it is hoped, provide a foundation on which a more complete survey can be based.

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