STUDY OF THE REDOX AND ACID-BASE PROPERTIES OF SODA-LIME SILICATE GLASS: APPLICATION TO THE HIGH TEMPERATURE CORROSION OF NICKEL-BASED ALLOYS AND CERAMIC MATERIALS

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by

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DECLARATION

I Hereby declare that I have conducted, completed the research work and written the dissertation entitled "Study of the Redox and Acid-Base Properties of Soda-Lime Silicate Glass: Application to the High Temperature Corrosion of Nickel-Based Alloys and Ceramic Materials". I also declare that it has not been previously submitted for the award for any degree or diploma or other similar title of this for any other examining body or University.

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LIST OF SYMBOLS

Symbols	Descriptions
E_a	Activation energy
a	Activity
β_a	Anodic kinetics constant
β_c	Cathodic kinetics constant
I_{corr}	Corrosion current density
E_{corr}	Corrosion potential
$V_{thickness\ loss}$	Corrosion rate (thickness loss)
V_{corr}	Corrosion rate (Stern-Geary)
ρ	Density
Ø	Diameter
k'_1	Linear constant
D*	Network oxygen diffusion coefficient
D	Oxygen diffusion coefficient
fO_2	Oxygen fugacity

k'_p	Parabolic constant
Rp	Polarisation resistance
S	Surface area
T	Temperature
t	Time
Λ_{th}	Theoretical optical basicity
η	Viscosity

LIST OF ABBREVIATIONS

BSE	Backscattered electron
DTA	Differential thermal analysis
EPMA	Electron probe micro-analysis
SEM	Scanning electron microscope
SE	Secondary electron
NCxS	Na_2O-CaO-xSiO_2 (Soda-lime silicate)
NxS	Na_2O-xSiO_2 (Soda silicate)
TGA	Thermogravimetric analysis
UV-Vis	Ultaviolet-visible spectroscopy
XRD	X-ray diffraction analysis

KAJIAN SIFAT-SIFAT REDOKS DAN ASID-BES KACA SODA-KAPUR SILIKAT: APLIKASI UNTUK KAKISAN BERSUHU TINGGI ALOI BERASASKAN NIKEL DAN BAHAN-BAHAN SERAMIK

ABSTRAK

Sifat kakisan aloi-aloi pembentuk kromia (Cr_2O_3) dan alumina (Al_2O_3) dalam leburan soda-kapur silikat dikaji dengan menggunakan teknik 'rendaman' yang disertakan dengan pengukuran elektrokimia. Gabungan kedua-dua teknik tersebut membawa kepada penentuan aspek-aspek umum kakisan oleh kaca terlebur serta tindakbalas redoks dan kinetik yang mengawal proses kakisan. Keputusan eksperimen mendedahkan bahawa Al_2O_3 tidak dapat memberikan perlindungan terhadap kakisan oleh kaca terlebur oleh kerana ia mempunyai keterlarutan yang tinggi di dalam leburan tersebut. Walau bagaimanapun, aloi pembentuk Cr_2O_3 dapat menahan terhadap kakisan oleh kaca terlebur jika aloi tersebut telah dilakukan rawatan pra-pengoksidaan dalam udara sebelum rendaman. Oleh kerana ketahanan lapisan Cr_2O_3 berkait dengan persaingan antara pembentukan oksida dan keterlarutannya dalam leburan, maka ciri-ciri fizikokimia Cr_2O_3 dalam kaca leburan seterusnya dikaji dengan mendalam bagi memahami pengaruh parameter yang berbeza terhadap had keterlarutan Cr_2O_3. Kajian telah dijalankan dengan mengambil kira pengaruh suhu (T), fugasiti oksigen (fO_2) dan komposisi kaca terhadap kebolehlarutan Cr_2O_3 dalam leburan. Kajian awal kinetik mendedahkan bahawa masa untuk mencapai keseimbangan berbeza bagi parameter tersebut. Walau bagaimanapun, masa keseimbangan kompromi dipilih untuk memuaskan semua masalah yang dihadapi. Kajian termodinamik menunjukkan bahawa pengaruh T dan fO_2 terhadap keterlarutan Cr_2O_3 dalam leburan soda-kapur silikat ternari (Na_2O-CaO-

$xSiO_2$) kelihatan koheren dengan leburan binari (Na_2O-$xSiO_2$). Walau bagaimanapun, keterlarutan Cr_2O_3 dalam leburan ternari adalah lebih rendah daripada leburan binari. Nilai keterlarutan Cr dalam Na_2O-CaO-$xSiO_2$ (x = 3, 4, 5 and 6) untuk suhu yang berbeza (T = 1200^{o}C, 1300^{o}C and 1350^{o}C) dan fugasiti oksigen yang berbeza ($-12 \leq \log fO_2 \leq -0.6$) berada antara 0.23 at.% hingga 1.09 at.%. Pengaruh kebesan dikaji terhadap leburan ternari dan binari dengan mengambil kira kebesan optik teori (Λ_{th}) dan aktiviti Na_2O. Nisbah redoks (Cr^{II}/Cr^{III} and Cr^{VI}/Cr^{III}) ditentukan melalui penghalusan matematik. Perbandingan dengan keputusan yang telah diperoleh dalam leburan binari dan penyimpangan dari nilai teori yang dijangkakan apabila melibatkan spesies kromium, menimbulkan andaian mengenai peranan yang dimainkan oleh CaO dalam mempengaruhi tindak balas yang melibatkan spesies daripada pasangan O^{2-}/O_2.

STUDY OF THE REDOX AND ACID-BASE PROPERTIES OF SODA-LIME SILICATE GLASS: APPLICATION TO THE HIGH TEMPERATURE CORROSION OF NICKEL-BASED ALLOYS AND CERAMIC MATERIALS

ABSTRACT

The corrosion behaviour of chromia (Cr_2O_3) and alumina (Al_2O_3) forming alloys in soda-lime silicate melts was studied by using 'raw immersion' technique which was coupled with electrochemical measurements. The combination of both techniques leads to the determination of the general aspects of the corrosion by the molten glass as well as the redox reactions and the kinetics that rule the corrosion process. The results revealed that Al_2O_3 is not able to provide protection against corrosion by molten glass since it has a high dissolution in the melt. However Cr_2O_3 forming alloy could resist against corrosion by molten glass if the alloy was subjected to a preoxidation treatment in air before the immersion. As the durability of the Cr_2O_3 layer is linked to the competition between the oxide growth and its dissolution in the melt, the physicochemical properties of Cr_2O_3 in molten glasses were then thoroughly studied in order to understand the influence of different parameters on the limit of Cr_2O_3 solubility. The works were conducted by taking into account the influence of temperatures (T), oxygen fugacities (fO_2) and the glass compositions on the solubility of Cr_2O_3 in the melts. The preliminary kinetics study revealed that the time to reach equilibrium varies with the parameters (T, fO_2 and glass compositions). However, a compromising equilibrium time was chosen in order to satisfy all the problems encountered. The thermodynamic study showed that the influence of T and fO_2 on the Cr_2O_3 solubility in ternary soda-lime silicate melts (Na_2O-CaO-xSiO_2) seems to be in coherence with the results in binary melts (Na_2O-

$xSiO_2$). Nevertheless, the Cr_2O_3 solubility in ternary melts is lower than in binary melts. The Cr solubility values in Na_2O-CaO-$xSiO_2$ (x = 3, 4, 5 and 6) for different temperatures (T = 1200^oC, 1300^oC and 1350^oC) and different oxygen fugacity ($-12 \leq \log fO_2 \leq -0.6$) lie between 0.23 at.% to 1.09 at.%. The influence of basicity was studied in these ternary and binary melts by taking into account the theoretical optical basicity (Λ_{th}) and the activity of Na_2O (aNa_2O). The redox ratios (Cr^{II}/Cr^{III} and Cr^{VI}/Cr^{III}) were determined through a mathematical refinement. The comparison with the results obtained in binary melts and the deviation from the theoretical values expected when speciation of Cr is involved, induce the assumption of the role played by CaO in influencing the reactions involving species from O^{2-}/O_2 couple.

ETUDE DES PROPRIÉTÉS ET ACIDO-BASIQUE DE VERRE SODO-CALCIQUE: APPLICATION À LA CORROSION HAUTE TEMPÉRATURE D'ALLIAGES BASE NICKEL ET DE MATÉRIAUX CÉRAMIQUES

RÉSUMÉ

Le comportement en corrosion d'alliage chromine (Cr_2O_3) et alumine (Al_2O_3) formeurs dans des verres sodo-calciques à haute température a été étudié en couplant des techniques électrochimiques avec la caractérisation post-mortem des matériaux immergés dans le milieu fondu. Les mécanismes réactionnels de la corrosion par ce type de milieu ont ainsi pu être abordés, de même que les aspects cinétiques. Les résultats ont montré que l'alumine n'était pas capable de protéger les alliages contre la corrosion, dans la mesure où sa solubilité dans le verre est particulièrement importante. Cependant, les alliages chromine formeurs ont montré de bonne propriété de résistance à la corrosion, dans la mesure où ceux-ci ont préalablement subi un traitement de pré-oxydation. Lors de l'immersion, une compétition entre la croissance de la couche de chromine et sa dissolution dans le verre s'installe, régissant ainsi la durée de vie de la couche d'oxyde protectrice. En conséquence, une attention particulière a été portée sur la physico-chimie de la chromine en milieu verre fondu. La solubilité de la chromine a donc étudiée afin de comprendre l'influence des paramètres température (T), fugacité en oxygène (fO_2) et composition du verre. Une étude cinétique préliminaire a permis de mettre en évidence l'influence de ses paramètres sur les mécanismes et le temps de mise à l'équilibre. D'un point de vue thermodynamique, l'influence des paramètres T et fO_2 sur la solubilité du chrome dans des verres ternaires Na_2O-CaO-xSiO_2 est cohérente avec les études antérieurement menées sur des verres binaires Na_2O-xSiO_2. Néanmoins, la solubilité

de la chromine est nettement plus faible dans le cas des verres ternaires. Les valeurs de la solubilité de Cr dans Na_2O-CaO-xSiO_2 (x = 3, 4, 5 and 6) pour différentes températures (T = 1200°C, 1300°C and 1350°C) et différente fugacité en oxygène (-12 ≤ log fO_2 ≤ -0.6) se situent entre 0.23 at.% à 1.09 at.%. L'influence de la basicité a été parallèlement étudiée dans les verres binaires et ternaires, en prenant en compte la basicité optique théorique (Λ_{th}) et l'activité en oxyde de sodium (aNa_2O). Les rapports redox (Cr^{II}/Cr^{III} et (Cr^{VI}/Cr^{III}) ont été déterminées suite à un affinement mathématique. La comparaison avec les résultats obtenus dans le cas des verres binaires ainsi que de grandes différences observées par rapport aux résultats théoriques dans le cas où la spéciation du chrome intervient laissent penser que l'oxyde de calcium CaO a une influence dans les réactions impliquant les espèces du couple O_2/O^{2-}.

CHAPTER 1

INTRODUCTION

In high temperature industries, most of the metallic parts normally consist of nickel-based alloys with high chromium and aluminium contents, which can lead to the formation of chromia, Cr_2O_3 and alumina, Al_2O_3 when in contact with air atmosphere at high temperature. These two oxides are very well known to provide good protection against oxidation as they usually form homogeneous and protective layers on the alloys.

The biggest challenge faced by the production of glass is related to the lifetime of the glass processing equipments which are in contact with molten glass. These equipments are expected to have the ability to withstand harsh environments and thus to resist against high temperature corrosion since they are normally consist of chromia (Cr_2O_3) forming alloys with chromium mass content ranging from 25 to 30 wt.%. However, the stability of these alloys in molten glasses, which is mainly governed by the dissolution of the protective chromia in the melts, is one of the crucial factors that determine the lifetime of these metallic parts.

During the last 20 years, the team "Surface et Interface : Réactivité Chimique des Matériaux" has been focusing on the corrosion of different materials in molten glass media. In a first approach, electrochemical methods has been used in order to characterise the corrosion behaviour of the metals/alloys in molten glass. The ability of the alloys to build a protective chromia layer has been emphasized as the best candidates for long term corrosion resistance in molten glass media. As a consequence, the works have been continued by a more specific study devoted to the behaviour of chromia in molten silicates. In this work, a focus has been given on the characterisation of the basicity of the media; a crucial property of the glass which gives a profound influence on the behaviour of chromia in the melt. A previous PhD work led by Sandra Abdelouhab has contributed to the development of the *in situ* measurement of the activity of the strong base, sodium oxide (Na_2O). This work proved the profound effect of different parameters on the corrosivity of molten silicates, *i.e.* temperature, oxygen fugacity and basicity. As a continuity, a second PhD work performed by Hichem Khedim, dealt with the study of the solubility of chromia in simple binary glasses (Na_2O-xSiO_2 system). Through this work a specific device has been developed, allowing the control of the temperature, oxygen fugacity and glass composition parameters independently.

The work proposed here is an extension of the study of the solubility of chromium in glasses whose basic composition is similar to the most common industrial glass. In this present work, an introduction of the calcium oxide (CaO) to the simple binary glass has been taken into account. The aim is to have a closer investigation towards a well-known corrosive system *i.e.* CMAS (CaO-MgO-Al_2O_3-SiO_2), which is directly involved in the corrosion of TBC (Thermal Barriers Coatings). In addition, CaO which is a basic oxide also behaves as a network modifier as Na_2O. Therefore, it is necessary to evaluate the effect of CaO addition to binary glassy matrix Na_2O-xSiO_2 on the physicochemical properties of the ternary system.

The present work is a continuity of the previous studies in the binary soda silicate Na_2O-$xSiO_2$ melts. The objectives of this work are (i) to evaluate the performances of chromia forming and alumina forming alloys in simplified soda silicate and soda-lime silicates in order to compare the ability of these oxides to give protection against corrosion in molten glasses (ii) to extend the knowledge of the physicochemical properties of chromia in simplified molten silicates of the Na_2O-$xSiO_2$ system by an addition of a second network modifier which is the basic oxide CaO. The manuscript is organised as follows:

Firstly, a literature review is proposed in the second chapter. A description of the molten glass media is given, in terms of structure, acid base properties, and redox properties. Then, the state of art on the corrosion of metals and alloys in molten glass is presented. Chromia and alumina forming alloys are thus emphasised. Then, a part deals with the previous studies devoted to the behaviour of chromia in silicate melts is presented in the final part of this chapter.

The materials and experimental methods used in this work are presented in the third chapter. The characterisation of the raw materials, alloys and glasses used in this study is detailed in Appendices. The specific electrochemical characterisation of the corrosion in molten media is detailed herein. The electrodes used in molten glass at high temperature are an adaptation from the methods used in aqueous media. The reactor allowing the independent control of temperature, oxygen fugacity and glass composition which has been developed in a previous oxide solubility study is also described in this chapter.

The fourth chapter is devoted to the determination of the corrosion of (i) chromia forming and (ii) alumina forming Ni-based simplified alloys in different types of silicate melts. A 'Raw immersion' test followed by a thorough observation of the samples give informations about the general aspects of the corrosion by the molten glass (surface morphology, glass penetration, thickness loss, oxide thickness, etc.). Correlation is then made with the electrochemical measurements, which allows an access to further information on the redox reactions and the kinetics ruling the corrosion process. An accurate comparison is made between chromia and alumina about their ability to give an efficient protection against glass corrosion.

Since the chromia has the ability to provide protection to the alloys due to its low solubility in molten glass, its physicochemical properties are then detailed in the fifth chapter. Firstly, the dissolution kinetics of chromia in different conditions (*i.e.* temperature, oxygen fugacity, melt composition are thoroughly studied herein. The aim is to choose the best duration of heat treatment in order to be as close as possible to the equilibrium, thus allowing a pertinent thermodynamic study. The mechanisms which are strongly correlated to the diffusion of oxygen species in the melt are also discussed.

The last part deals with the solubility of chromia in the ternary system Na_2O-CaO-$xSiO_2$. The influences of temperature and oxygen fugacity are first observed, in the same way as in the previous study performed in binary melts. Then, a specific attention is paid on the role played by CaO in the melts, and its influence on the physicochemical properties of the Cr oxo-complex species.

CHAPTER 2

LITERATURE REVIEW

Introduction

This chapter is devoted to a brief description of the physicochemical properties behind the word 'glass' as well as the corrosion phenomena occurring in molten glass. The prerequisite for this attempt is to have an understanding of the structure and the components of the glass which will be discussed in the first part. Secondly, the theoretical and experimental of the concept of acid-base in molten glass as well as the redox reactions in the melts will be discussed thoroughly through a synthetic review of the state of art of many previous studies. The phenomena of corrosion of metals and alloys in molten glasses will be described in the next part. As the protection of the alloys in molten glasses is related to the nature and stability of the oxide layer formed at the interface alloy/glass, hence the physicochemical behaviour of some important oxides in molten glasses will be presented in the final part.

2.1. General aspects of glass

The silicate glass has become a high-tech material with numerous applications in various fields including industry (aeronautic, power generation, glass fibre elaboration, etc.), architecture, arts and as very recently, in waste management's with the use of glass matrices for the stabilisation and the storage of nuclear waste. The term 'glass' brings many contradictions among scientists whether it should be classified as a solid or as a liquid. However, by considering the definition behind the term 'glass', it actually refers to a state of matter, usually produced when a viscous molten material is cooled rapidly to below its glass transition temperature, with insufficient time for a regular crystal lattice to form. Being neither a liquid nor a solid, but sharing the qualities of both, glass possesses its own state of matter which is called an amorphous solid. Unlike crystals, glass does not have a sharp melting point and does not cleave in preferred directions. Glass also shows elasticity like crystalline solids. Thus, instead of describing the glass by its definition, it is more appropriate to define it by considering the physicochemical properties of the glass itself which strongly depend on its structure.

2.1.1. Formation and structure of silicate network

Unlike crystal (Figure 2.1(a)), glass is a three-dimensional network of atoms forming a solid that lacks periodicity or ordered pattern (Figure 2.1(b)). Random atomic arrangement as would appear in a sodium silicate glass has been shown schematically in Figure 2.1(c). In this case, a Si^{4+} acts as the building block of the glass network which is known as a network-forming cation (NWF)[1]. The four positive charges of the silicon ion tend to form bonds with four oxygen atoms, forming SiO_4 tetrahedra *i.e.* four-sided pyramidal shapes, connected to each other at the corners. An oxygen atom that connects two tetrahedra is known as bridging oxygen while the oxygen atom which joins to only one silicon atom is called a non-bridging oxygen. In the example of sodium silicate glass (Figure 2.1(c)), a univalent sodium ion (Na^+) occupies an interstice adjacent to the SiO_4 tetrahedra in order to balance the remaining negative charge. The role played by Na^+ in the silicate network will be discussed thoroughly in the next part. This corner-sharing tetrahedral structure achieves a liquid-like randomness rather than a crystalline regularity because of the random value of the Si-O-Si angle. Furthermore, there are twist angles arising between two connected tetrahedra.

Glass consists of network formers, network modifiers and intermediates[1,2]. In order to predict the oxides that tend to form glasses, Zachariasen[3] has proposed four rules for glass formation:

- No oxygen atom may be linked to more than two cations.
- The cation coordination number is small: 3 or 4.
- Oxygen polyhedra share corners, not edges or faces.
- For 3D networks, at least three corners must be shared.

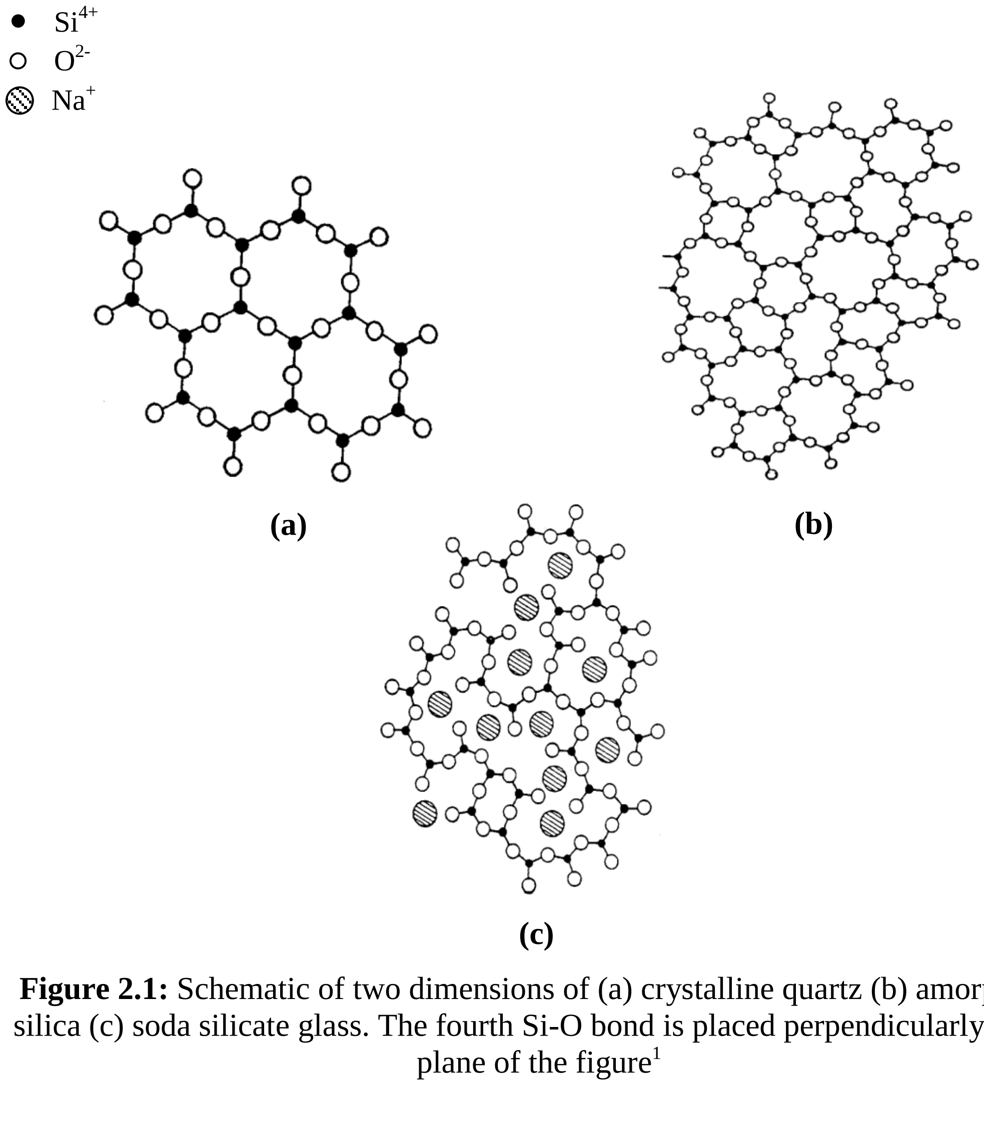

Figure 2.1: Schematic of two dimensions of (a) crystalline quartz (b) amorphous silica (c) soda silicate glass. The fourth Si-O bond is placed perpendicularly to the plane of the figure[1]

Apart from Zachariasen[3], Sun[4] has also introduced a correlation between the strength of the interatomic bonds and the ability of the material to form a glass. The classification of the substances with regard to their glass-forming ability has become the most important contribution of Sun's single bond criterion. Dietzel[5] has proposed to characterise the ability of the cations to form a network with oxygen ions by the Coulomb's force of attraction. It is known as the 'field strength' and can be described by the following equation:

$$A = \frac{Z_c}{(r_c + r_o)^2} \tag{2.1}$$

where Z_c is the cation valence, r_c and r_o are the cation and O^{2-} radii respectively and expressed in Å. The values of the field strength (*A*) for various cations are presented in Table 2.1. The value of $A > 1.0$ represents the cations of the network formers whereas $A < 0.35$ corresponds to the cations of the network modifiers.

Table 2.1: The field strength of various cations[5]

Elements	$\mathbf{Z_c}$	$\mathbf{r_c}$	$\boldsymbol{A = \frac{Z_c}{(r_c + r_o)^2}}$	
P	5	0.31	1.710	Cation formers
V	5	0.49	1.400	
Si	4	0.40	1.235	
B	3	0.25	1.102	
Sb	5	0.74	1.092	
Ge	4	0.53	1.074	
Ti	4	0.74	0.873	Cation intermediates
Al	3	0.53	0.805	
Zr	4	0.86	0.783	
Be	2	0.41	0.610	
Mg	2	0.86	0.392	
Zn	2	0.88	0.385	

Table 2.1: Continued[5]

Elements	**Z_c**	**r_c**	$A = \dfrac{Z_c}{(r_c + r_o)^2}$	
Ca	2	1.14	0.310	Cation modifiers
Pb	2	1.33	0.268	
Li	1	0.90	0.189	
Na	1	1.16	0.153	
K	1	1.52	0.117	

2.1.1.1. Network formers

According to Zachariasen[3], the cations which have the coordination number of 3 or 4 could readily form glasses and are commonly known as 'network formers' as they provide the backbone in other mixed-oxide glasses. However, this rule is not applicable for all cases. For example, Al_2O_3 is not able to form glass when the oxide is alone since the charges are not sufficient to form a stable polyhedron with four oxygen. The examples of network formers are B_2O_3, SiO_2, P_2O_5 and GeO_2.

2.1.1.2. Network modifiers

Alkali and alkaline-earth elements such as Li, Na, K, Ca and Mg play a role as a network modifiers in the glass network[2]. A network former such as SiO_2 is well-known for its high melting temperature which lies between 1600^{o}C - 1725^{o}C. At this temperature, the liquid is very viscous, making the processing of the glass difficult. Since the network modifiers have the ability to break up the covalent bonds between the network formers and the anions, a network modifier such as Na_2O which is known as a 'flux' is always added to the network formers such as SiO_2 in order to decrease the melting temperature of pure SiO_2 and also the viscosity of the melts.

There are two important effects by an addition of Na_2O to the network. Firstly, every Na_2O molecule will disrupt the network and will cause the formation of two groups of $Si-O^{-}Na^{+}$ (Figure 2.2). The oxides that have the ability to modify the network are called 'network modifiers' since they can transform the bridging oxygen (the oxygen that links to two cation formers) into non-bridging oxygen (oxygen which links to only one cation former). The breaking of the Si-O bonding lowers the viscosity of the melt, thus facilitating the fusion process. Secondly, an alkali oxide such as Na_2O has the ability to lower the liquidus temperature of the melt, thus limiting the risk of devitrification phenomenon.

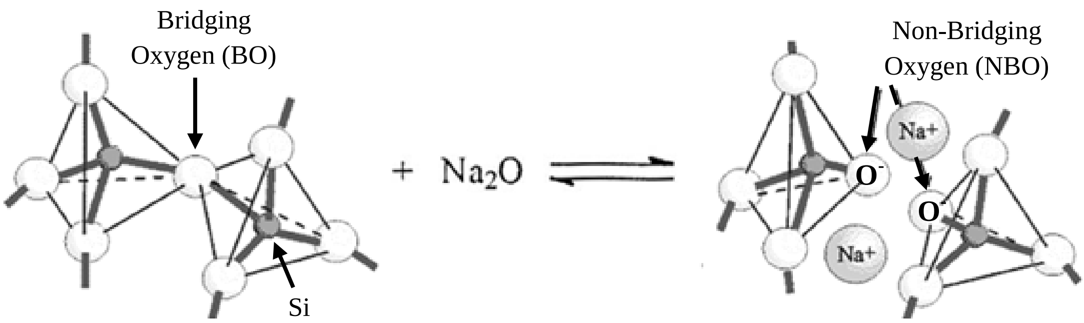

Figure 2.2: Schematic of the breaking of Si-O bonding by introducing a Na_2O molecule in the silicate network[2]

2.1.1.3. Intermediates

The intermediate oxides are less clearly defined compared to the network formers and network modifiers. The intermediates may act as network formers or network modifiers depending on the glass compositions. The oxides such as Al_2O_3, BeO, MgO and ZnO are examples of the intermediates[2]. The intermediate cations create a slightly covalent binding with the O^{2-} anions. The coordination tendency of these ions is insufficient to establish a three-dimensional network. Since the intermediates can establish a bond with two or three oxygen ions, the addition of intermediates to a silica glass does not lead to a complete breaking up of the polyhedra network. The presence of the intermediates suppresses the tendency of the glass melt to form crystals during cooling.

2.1.1.4. The role of CaO

CaO is an alkaline-earth oxide playing a role as a glass modifier since it also breaks the Si-O bonding in the network[2]. The introduction of CaO into the network could be described by the following equation:

$$\equiv Si - O - Si \equiv + CaO \rightarrow \equiv Si - O^{-} Ca^{2+} O^{-} - Si \equiv \tag{2.2}$$

An addition of CaO to the network leads to the creation of two non-bridging oxygen. It can also decrease the viscosity of the molten glass but the effect is more moderate compared to the addition of alkali oxide. Furthermore, the effect of an addition of alkaline-earth oxide on the decreasing the liquidus temperature of the silicate network is less significant compared to the alkali oxide since the alkaline-earth oxides are more refractory compared to the alkali oxide.

In the case of soda-lime silicate glass, an addition of CaO will break the bridging of Si-O-Si bonds between silicate tetrahedron, thus decreasing the average silicate chain length. However, the electronic charge of calcium ion which is higher than sodium ion makes the $[SiO_4]^{4-}$ to be more easily associated with Ca^{2+} ions compared to the monovalent cation. Therefore, the Na^{+} ions are potentially freer in the Ca-bearing system relative to the sodium-silica binary. According to Abdelouhab *et al*.[6], the increased number of non-bridging oxygen in the Ca-bearing system (Na_2O-CaO-xSiO_2) may lead to an increase in the Na_2O activity relative to that observed in the equivalent Na_2O-xSiO_2 melt. Addition of CaO to a binary alkali silicate glass is known to increase its durability[1]. They are chemically durable against water and acid and have fairly good weathering resistance. However, soda-lime silicate glass has high thermal expansion, thus prone to thermal shock failure.

2.1.1.5. The role of Al_2O_3

Al_2O_3 will never form glass itself but acts like a glass former or modifier if combined with other oxides[2]. Therefore Al_2O_3 is classified as an intermediate in the glass network. By introducing in the pure SiO_2, Al^{3+} has the coordination number of VI, thus playing a role as a network modifier. Al_2O_3 has the ability to be a network former in the alkali-containing glasses when Al^{3+} substitutes Si^{4+} in the network. Every Al_2O_3 introduced in the melt will remove a pair of non-bridging oxygen (associated with two Na^+ which must neutralise the two $[AlO_4]^{5-}$ tetrahedra) which leads to an increase of the glass viscosity due to the formation of aluminate tetrahedra[7]. However, the structural role of the Al^{3+} in alkali silicate glasses depends on the aluminium concentration and the temperature of the melts[8].

2.1.2. Acid-base properties in glass melts

As in the aqueous media, the acid-base properties play an important role in the molten glass for the theoretical understanding of the nature of some physicochemical processes in glass-forming melts and slags, as well as for applied tasks, *e.g.* the prediction of the process tendencies and design of the materials with necessary characteristics. Acid-base properties of the glass also show a significant influence on the corrosion of metal/alloys by molten glasses[9–11]. A large number of studies have been performed in order to reveal the theories of acid-base in the molten glass[12–19] as well as to determine a scale to distinguish the acidity or basicity of the melts.

2.1.2.1. Acid-base concepts in glass melts

The Brönsted-Lowry[12,13] theory provides a broader definition of acids and bases in a protonic solvent. According to this theory:

- An acid is defined as a species which has the tendency to yield a proton.
- A base is a substance that can accept a proton.

The Brönsted-Lowry theory still does not present the full generalisation of acid-base phenomena. This theory does take into account the experimental fact that there are many substances besides the hydroxyl ion which exhibit typical basic properties, but fails to recognise complementary data with regard to acids. Therefore, the proton transfer acid-base theory has practically no application in glass.

As a contrary, Lewis[14] theory considers acid-base functions and related processes independently of the solvent. According to Lewis:

- An acid is any species that is capable of accepting a pair of electrons to form a covalent bond by sharing with the electron donor.
- A base is any species that can donate a pair of electrons to form a covalent bond with the acid.

Although it can overcome many difficulties in aqueous solution, the application of Lewis theory in glass melt raises doubt since there is a close relationship between acid-base function and oxidation-reaction in the molten glass. Even though both acids and oxidising agents tend to accept electrons, however the acid accepts electron pairs and forms coordinate covalent bonds whereas the oxidising agent keeps the electrons to itself.

The concept of acid-base in molten oxides was first introduced by Lux[15] in 1939. His definition can be represented by the following equation:

$$\text{Base} = \text{Acid} + O^{2-} \tag{2.3}$$

The concept of Lux was developed by Flood and Förland in 1947[16] and remains actual up to the present time. Flood and Förland have summarised that the acid-base in an oxide system is characterised by the transfer of an O^{2-} ion from one state of polarisation to another. The degree of basicity of an oxide is determined by the ability of oxygen atoms to give up electrons. The basicity is greater when the O^{2-} ion is unaffected by surrounding cations. As a summary of Lux and Flood theory in the case of molten oxides and molten salts, the exchange of O^{2-} ions between the base and the acid can be assimilated to the exchange of electrons in the Lewis theory. A strong base is capable of combining with electron acceptor which is known as oxoacid. The species resulting from these combinations are called oxobase. For example:

- Metal oxides (Na_2O, BaO, Al_2O_3, ...) are bases and metal cations (Na^+, Ba^{2+}, AlO^+, ...) are conjugate acids.
- Oxoanions (SiO_3^{2-}, SO_4^{2-}, CO_3^{2-},...) are bases and the oxides (SiO_2, SO_3, CO_2,...) are conjugate acids.

These couples react according to the following equilibrium:

$$\text{oxobase} \rightleftharpoons \text{oxoacid} + O^{2-} \tag{2.4}$$

The equilibrium constant, K:

$$K = \frac{a_{acid} \times a_{O^{2-}}}{a_{base}} \tag{2.5}$$

will be a measure of the strength of the acid-base pair.

By analogy with the aqueous solution where the H^+ ion activity allows to establish an acidity scale (pH = -log $a(H^+)$), the activity of O^{2-} ions has been used as a basicity indicator in the molten glass[15,17,18] or in a medium where the O^{2-} ions exist as free ions according to the following equation:

$$pO^{2-} = -\log a(O^{2-}) \tag{2.6}$$

where $a(O^{2-})$ is the activity of the oxide ions in the medium. It is noteworthy that the pO^{2-} scale works in the reverse direction as compared with the pH scale in protonic solvents. In contrary with the case of aqueous solution where the standard state of H^+ ion can be defined precisely (water is a universal solvent), no standard state can be defined for molten glass because the composition of the solvent varies from one glass to another. Furthermore, the basicity of the oxide melts depends on the force of the ionic bonding between O^{2-} and the cation modifier[1]. The basicity increases with the increase in ionic radii of the alkali ions and alkaline-earth ions. Therefore, the basicity increases by descending the column of alkali and alkaline-earth elements and decreases by going through the group of alkali and alkaline-earth in the periodic table. Since the terms "acidity" and "basicity" are determined via O^{2-} activity, both characteristics become indiscernible. Therefore, the boundary dividing "acid" and "base" in melts is a problem of standardisation and quantitative of pO^{2-} measurement[19].

2.1.2.2. Evaluation of acid-base properties in molten glass

The acid-base properties in the molten glass have been defined through theoretical and calculation models by several authors. Moreover, some efforts have been made in order to measure the basicity of the molten glass through *ex situ* and *in situ* measurements.

(a) Theoretical models of calculation

Many studies have been devoted to develop theoretical models of calculation of acid-base properties in molten glass in order to quantify the activity of oxide ion (O^{2-}) and the activity of non-bridging oxygen as a function of glass composition.

➢ *Model of Sun*

In 1948, Sun[20] estimates the strength of cation-oxygen bonding by the formation enthalpy of the glass. The strength of cation-oxygen bonding depends on the dissociation energy of the oxides in the molten glass and the coordination of oxygen with the cation. According to this model, an acid is a network former which has a high electron affinity. Cameron[21] has proposed to calculate the glass basicity based on the value of oxides basicity from Sun[20]. The basicity of boric oxide has been randomly chosen as the origin of the scale. The glass basicity is proportional to the basic number « B »:

$$a(O^{2-}) = Cst \times B \tag{2.7}$$

where

$$B = 119 - \left(\frac{A_{Sun(oxideA)} \times \%mol}{100} + \frac{A_{Sun(oxideB)} \times \%mol}{100} + \ldots \right) \tag{2.8}$$

The basicity value of oxides (A_{Sun}) which has been proposed by Sun is compiled in Table 2.2:

Table 2.2: The values of A_{Sun} allowing to determine the acid-base properties of the glass[20]

Oxides	$\boldsymbol{A_{\mathrm{Sun}}}$
K_2O	13
Na_2O	20
BaO	33
Li_2O	36
MgO	37
PbO	36-39
Al_2O_3	53-67
Sb_2O_3	68-85
B_2O_3	119
As_2O_3	70-87
SiO_2	106

➢ *Model of Sanderson*

Sanderson[22–25] has proposed a model to calculate the acid-base properties in the glass by considering a magnitude (*x*) which is attributed to the size of an atomic electron density. The magnitude *x* can be related to the Pauling electronegativity (χ) by the following equation:

$$x = \frac{\sqrt{\chi} - 0.77}{0.21} \tag{2.9}$$

For an oxide M_mO_n, the value x can be calculated according to the following equation:

$$xM_mO_n = \left[(x_M)^m (x_O)^n \right]^{\frac{1}{m+n}} \tag{2.10}$$

Thus, the acidity/basicity of the glass A_{glass} can be determined by the following equation:

$$A_{glass} = (x_1^{N_1} \times x_2^{N_2} \times ..... \times x_n^{N_n} \times 5.02)^{\frac{1}{(N_1+N_2+....+N_m+1)}} \tag{2.11}$$

where x_i is the Sanderson electronegativity of element i, and N_i is the total number of oxygen in the system.

➢ *Model of Toop and Samis*

In 1962, Toop and Samis[26] have proposed the existence of three different forms of oxygen:

- The bridging oxygen which links to two silicon atoms (O^0).
- The non-bridging oxygen which links to one silicon atom (O^-).
- The free oxide ion (O^{2-}).

It is possible to develop an equilibrium between these three forms of oxygen and thus to derive the equilibrium constant as expressed by the following equations:

$$2O^- \Leftrightarrow O^0 + O^{2-} \tag{2.12}$$

$$K = \frac{a(O^{2-}) \times a(O^0)}{a(O^-)^2} \tag{2.13}$$

The value of K is constant for a given temperature and it represents the characteristic of cations present in the molten glass. In this equation, Toop and Samis have replaced the activities of the components by their concentrations, hence specified the equilibrium proportions for each form of presented oxygen. For a molten oxide with a composition nM_2O-$(1-n)SiO_2$, the number of moles of oxygen atoms bonding to silicon atoms 4(1-n) can be written as the following equation:

$$2N(O^0) + N(O^-) = 4(1-n) \tag{2.14}$$

where $N(O^0)$ and $N(O^-)$ are the number of bridging and non-bridging oxygens. Thus, the following equation can be derived:

$$N(O^0) = \frac{4(1-n) - N(O^-)}{2} \tag{2.15}$$

The number of free oxide ions can be represented by the following equation:

$$N(O^{2-}) = n - \frac{N(O^-)}{2} \tag{2.16}$$

Since the reaction of one mole of oxide modifier with silica gives rise to two moles of non-bridging oxygen, the equilibrium constant between the three forms of oxygen can be written in assimilating the activities with their concentrations:

$$K = \frac{N(O^{2-}) \times N(O^0)}{N(O^-)^2} \tag{2.17}$$

By replacing the $N(O^{2-})$ *and* $N(O^{0})$ by Eq. 2.16 and Eq. 2.15 respectively, the following equation can be derived:

$$K = \frac{[(4-4n)-N(O^{-})]\times[2n-N(O^{-})]}{4N(O^{-})^{2}} \tag{2.18}$$

Eq. 2.18 can be simplified by the following equation:

$$(4K-1)\times N(O^{-})^{2}+(4-2n)N(O^{-})+8(n^{2}-n)=0 \tag{2.19}$$

The resolution of this equation for various values of equilibrium constants and for different stoichiometries allows the determination of the distribution of the three forms of oxygen present in the melt under the considered environment. However, Konakov[19] has pointed that the states of O^0 in SiO_2 and the formed silicates, as well as O^- in these silicates, are indiscernible. Therefore, the Toop and Samis model was rather limited and could not be used for an adequate description of the acid-base interactions in real oxide melts. However, the approach by Toop and Samis was partly used in many known models[1,27,28].

(b) Experimental measurements

Due to the importance of the knowledge of acid-base properties in the molten glass and the difficulties in predicting it, many authors have developed some techniques in order to measure experimentally the acid-base properties in molten glass.

➢ *Gaseous solubility*

The relative basicity of molten glass can be evaluated experimentally by the solubility of certain gases (H_2O[29,30], CO_2[31–33], SO_2[34]) which dissolve in the glass network. The solubility of the gas will increase at any constant pressure of oxygen as the oxygen ion activity in the melt increases. Since the oxygen ion activity is related to the basicity of the melt, an increase in the solubility of the gas can be used as an indicator of an increase in the basicity of the melt.

➢ *Transition metal ions as acid-base indicators*

Paul and Douglas[35–37] have proposed a method by using transition metal ions as acid-base indicators in glass. The transition metals which have been introduced in molten glass behave like a Lewis acid and interact with the free oxide ions in order to form an oxocomplex. The possibility of using transition metal ions as indicators in silicate glasses is due to the fact that the coordination symmetry of these ions changes with the basicity of the melt. Due to their incompletely filled inner shell, the oxocomplex formed can be studied thoroughly by spectroscopic and magnetic measurements. The cations that are widely used in this method are Ni^{II} [35],Co^{II} [36] and Cr^{VI} [37]. In the case of Ni^{II} and Co^{II}, a change of coordination from octahedral symmetry to tetrahedral symmetry with increasing basicity can be determined by spectroscopic measurements since the optical absorption characteristics of octahedral and tetrahedral are distinctly different.

➢ *Transpiration method*

Since basicity of the melt links to the content of network modifiers in the glass, the transpiration method is dedicated to determining the activity of sodium oxide ($a(Na_2O)$) which plays a role as a network modifier by measuring the vapour pressure of the distillation gas of the molten oxides. Rego *et al.*[38] have used the transpiration technique to measure the vapour pressures of Na above the stirred Na_2O-$xSiO_2$ melts which are in equilibrium with graphite crucible and CO. The experiments have been performed at 1300°C and 1400°C for silica-rich melts under a system pressure of one atmosphere. Under these reducing conditions, the expected reaction is:

$$Na_2O_{(l)} + C_{(s)} = 2Na_{(g)} + CO_{(g)} \tag{2.20}$$

The equilibrium constant for the above reaction allows the determination of the activity of Na_2O in the silicate melts according to the following equation:

$$\log(a_{Na_2O}) = \log[(p_{Na})^2 \times p_{CO}] - \log K \tag{2.21}$$

The quantity $\log[(p_{Na})^2 \times p_{CO}]$, which is related to the $a(Na_2O)$ is plotted as a function of compositions for each two temperatures. The second-order curve fits give an access to the log K values, thereby allowing the determination of aNa_2O by the following equations:

at 1300°C,

$$\log a_{Na_2O} = -9.86 + 6.22 X_{Na_2O} + 6.75 (X_{Na_2O})^2 \tag{2.22}$$

and at 1400°C,

$$\log a_{Na_2O} = -9.01 + 2.44 X_{Na_2O} + 11.8 (X_{Na_2O})^2 \tag{2.23}$$

where X_{Na2O} is the mole fraction of Na_2O in the glass. An extension of this work, using an encapsulation technique to study the Na_2O-CaO-SiO_2 and Na_2O-MgO-SiO_2 systems and some synthetic blast-furnace slags have been described by Rego *et al*.[39] in another work.

- *EMF measurement*

The oxygen ion activity of two melts can be compared by measuring the difference of the electrochemical potential of oxygen in the melts. The only direct method by which oxygen ion activities can be compared independently without interference from other reactions is through an electromotive force measurement (EMF)[1]. This method requires the use of a reversible oxygen electrode immersed in molten glass. Thus, a platinum electrode which has been flushed by air is the best candidate for this type of application. It is also necessary to provide a bridge between the glasses being compared which has negligible junction potential. The basicity of the molten glass has been determined by measuring the different potentials between the working melt (studied melt) and the reference melt (melt with well-known basicity). The junction between the two glasses is ensured either by a β alumina[6,40–42] refractory or by a direct contact between these two glasses through a small diameter of orifice[43,44].

The potential generated by the electrochemical cell of type:

Platinum $O_{2(g)I}$	$Glass_{(I)}$	Ionic junction	$Glass_{(II)}$	Platinum $O_{2(g)II}$

is given by the following equation if $O_2(Pt)_I = O_2(Pt)_{II}$:

$$\Delta E = \frac{-RT}{2F} \times \ln \frac{a\left(Na_2O\right)_{(II)}}{a\left(Na_2O\right)_{(I)}} \tag{2.24}$$

where $Glass_{(I)}$ is the reference glass and the $Glass_{(II)}$ is the working glass. The Eq. 2.24 can be expressed as:

$$\ln a\left(Na_2O\right)_{II} = \ln a\left(Na_2O\right)_{I} - \frac{2F\Delta E}{RT} \tag{2.25}$$

This method allows a direct access to the relative basicity of a molten glass. Unlike the other methods which have been discussed before, the EMF measurement allows the determination of the basicity of the molten glass without modifying the solvent by an addition of gas or an indicator. Furthermore, a wide range of glass compositions can be studied using this technique especially for a higher acidity melt where the conventional method such as gas dissolution may not give an accurate result.

The activity of Na_2O in Na_2O-SiO_2 and Na_2O-CaO-SiO_2 systems has been measured by Neudorf and Elliott[40] by using this method. It has been demonstrated that an addition of CaO to the binary Na_2O-SiO melt causes an increase in the activity of Na_2O. The experimental activity data seems to have a good agreement with the values calculated using Richardson ideal mixing model[40].

The EMF measurement has been also applied by Abdelouhab *et al.*[6] in order to quantify the activity of Na_2O in a series of sodium-bearing silicate melts at high temperature. Abdelouhab has tried to make a comparison between the log a(Na_2O) obtained via EMF measurement and the calculated basicity using theoretical model