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The Solubility of Specific Metal Oxides in Molten Borate Glass

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Abstract

The solubility of Co_3O_4, Cu_2O, CuO, NiO and Mn_2O_3 in molten B_2O_3 and Na_2O-$2B_2O_3$ has been studied at a temperature of $900^{O}C$ under static conditions. The concentration of the dissolved metal oxides were determined by X-EDS and XPS elemental analysis. Uniformity of metal distribution has been confirmed using X-EDS and backscatter electron image mapping. It was found that the solubility of all metal oxides increased significantly with Na_2O content in the B_2O_3 solvent. The impact of a temperature increase of $150^{O}C$ and the influence of K_2O doping were evaluated and found to not cause any significant change.

I. Introduction

Extraction of high value or critical metals from waste sources, such as scrap electronics and portable power sources is of high interest.[1, 2] Traditional methods currently available are either pyro- or hydro-metallurgical based,[3] often adapted from minerals processing operations (MPO).[4] MPO methods are usually focused on one or two elements (i.e. Li and Co only), thus overlooking the possibility of other valuable metal recovery from scrap materials.[5] Moreover, a majority of these processes produce a large amount of waste, using water or water-based solutions.[6–9] For these reasons, currently available methods are not economically viable for a wide range of materials.

Molten salts provide a diverse range of uses such as extraction,[10] purifying,[11] and coating.[12] Borates are of high interest, yet mainly have been used in boronation[13–15] and glass forming,[16, 17] and have the ability to dissolve significant quantities of metals. However, the thermodynamic properties are not yet well understood and literature evaluating their behaviour is sparse. Williams et al.[18] have measured the influence of Na_2O on the solubility of various metal oxides in the borate salts. Borates provided good solubility of metals, which take the most thermodynamically stable form of their respective metal oxides in the solution. It has been concluded that the distribution coefficient (K_D) of metal ions between sodium chloride and sodium borate (at 927^{O}C) has a maximum value at around 25 mol% of Na_2O. Addition of SiO_2 also increased K_D, while P_2O_5 had no effect on the distribution coefficient.

Williams et al.[18] study of $NaCl-Na_2O-B_2O_3$ salts suggested they are capable of dissolving significant quantities of metal species. A method of metal extraction from waste using borates is proposed in this paper. In this method, waste feedstock is melted and dissolved in a molten borate solvent. All organics are pyrolysed, moisture evaporates, and impurities are dissolved. As a side effect, liquid materials in the molten slag materials experience an undercooling before solidification.[19] It has been reported to work efficiently as an extraction method with Nd (over 25 wt% solubility) and Sm (over 58 wt% solubility) while using scrap metal (i.e. magnets) as an input.[20, 21] Recovered metals can be subsequently extracted by electrochemical reduction.[22] Further work on other valuable metals such as Co has been suggested.[20] Borates inherent high resistance to water and other pollutions enables the processes to work under atmosphere in an open crucibles, which further makes the process easier and more viable.[23] These properties provide a good ground for molten salt based metal recovery processes.

In this paper a method is proposed for extracting metals using the B_2O_3 based salt as the solvent. A critical metal – cobalt is considered, as well as metals of significant economic importance – copper, nickel and manganese. Influence of two alkali metal oxides - Na_2O and K_2O, on the metal oxides solubility is evaluated. The investigation is focused on 900^0C with the aim of finding a compromise between efficiency and not overly high temperature for the potential metal extraction process.

II. Experimental Section

Pellets have been formed from metal oxide powders [NiO (99,8 %, <50 nm particle size), Co_3O_4 (99,5 %, <50 nm particle size), CuO (98 % <425 μm particle size), Mn_2O_3 (99 %, <44 μm particle size) from Sigma-Aldrich® by compressing (~1 tonne for 1 minute using a 13mm diameter die) and then sintering in a muffle furnace in air. The NiO preform was sintered in 800^{O}C for 5h, Co_3O_4 in 900^{O}C for 5h, Mn_2O_3 in 900^{O}C for 17h and CuO in 1050^{O}C for 4h, each one on a separate recrystallised alumina boat to avoid cross-contamination. The last step was a furnace cooling until the room temperature was reached. Cu_2O (>99 %) pieces were obtained by oxidizing copper rod (5 mm) in 900^{O}C in air. Sintering variables were chosen due to the variable thermal properties of the chosen materials. The pellets have been cut as necessary with a high-speed precision saw using a high density diamond blade.

The dissolution studies took place in platinum crucibles (Ögussa®, Pt/Ir 3 % mini crucible), filled with either B_2O_3 (Alfa Aesar, 99 %), $B_4Na_2O_7$ (Sigma-Aldrich, ≥99.5 %) or $B_4K_2O_7$ (Sigma-Aldrich, ≥99.5 %) depending on the test procedure. The amount of metal oxide placed in the crucible was based on the saturation concentration predicted using the thermodynamic equilibrium package available in the FactSage software [FactSage™ 6.4, FToxid database was used]. However, the lack of the experimental data for this system makes the simulation unreliable. Thus the obtained values were increased in order to provide enough material for the dissolution. Crucibles filled with the test materials have been placed in holders handmade from thermal bricks and placed in a muffle furnace. The procedure is represented by the flowchart shown in the *Fig. 1*.

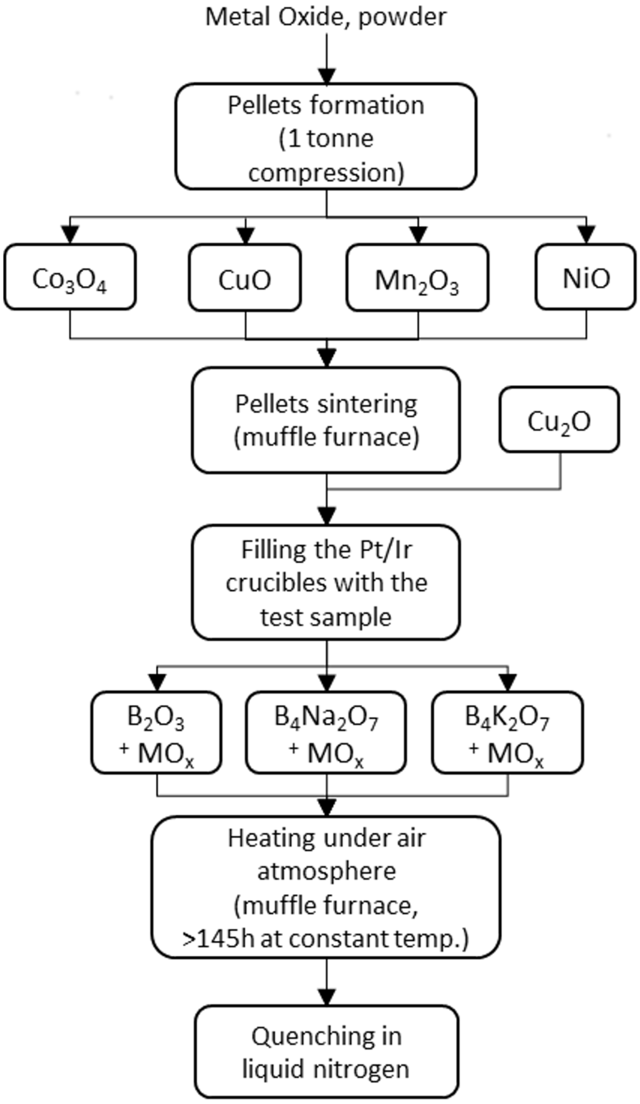


Fig. 1. Test procedure flowchart

The thermal cycle introduced during the experimentation is essential to avoid the borate salt foaming and being ejected from the test vessel. Borate-rich salts have been reported as likely to creep out of the containers and thus challenging to study.[24] In the present study, the author overcame the problem by introducing a slow heating regime with a dwell step, therefore minimising the apparent foaming effect and suppressing the salt creep. The samples were pre-heated to 480^{O}C at a heating regime of 2^{O}C/min, it was then kept at constant temperature for 60 minutes, and then heated to the final testing temperature (900^{O}C and 1050^{O}C), at a rate of 3^{O}C/min. No mass loss has been observed after the slow heating regime had been introduced. The heating procedure used for experimentation is given in *Fig. 2*.

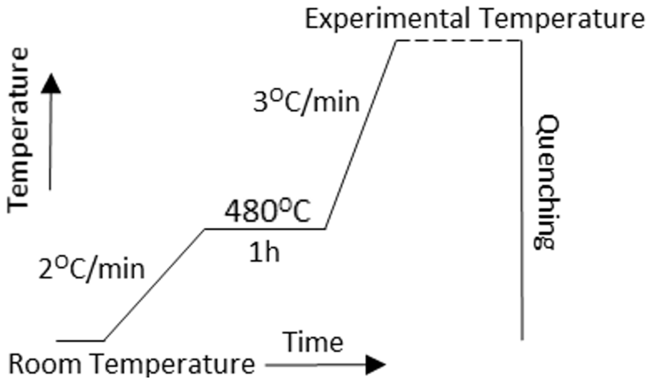


Fig. 2. Temperature profile of the experiment

For the samples to reach equilibrium, they have been kept in constant temperature of 900^{O}C or 1050^{O}C for at least 145 hours. After that time, samples were quenched in liquid nitrogen to immediately stop the process and avoid precipitates formation. No atmosphere control was enforced, leaving the crucibles open to air, as in other similar studies.[18]

The quenched glass samples were analysed using FEG-SEM (Carl Zeiss Gemini®) with X-ray Energy Dispersive Spectroscopy (X-EDS, Oxford Instruments®) and Electron Backscatter Diffraction (EBSD). This analysis was used to assess the metal distribution and concentration. X-EDS determines presence and quantities of chemical elements by detecting characteristic X-rays emitted from atoms. X-rays are released as a result of a beam of accelerated electrons hitting the atoms present in the sample undergoing analysis. The chemical identification is based on the energy of the X-rays emitted. Precise quantitative analysis is challenging with this apparatus due to the high concentrations of oxygen and boron elements in the samples which causes detection difficulties. Backscatter electron image mapping was used to confirm the uniformity of metal distribution in the sample, which indicates that the sample had reached the equilibrium state and the metal concentration is uniform throughout the glass. X-Ray Photoelectron Spectroscopy (Axis Ultra DLD, Kratos®) has been used to confirm the solubility in the Na_2O doped samples. The XPS analyses electrons ejected from an electron shell of an atom after the atom absorbs an X-ray photon. The biding energies of atomic electrons have characteristic values, which allows for identification of chemical elements present in the sample. Quantification with XPS and X-EDS methods is possible due to the detection peak intensity being related to the chemical concentration.[25]

III. Results and discussion

It should be noted that the samples were open to air by design, thus the oxygen fugacity was not controlled but set by the ambient conditions at the experimental temperature. Thermodynamic study was done with the use of the FactSage™ thermodynamic suite (“*Reaction*” module)[26] to evaluate the metal oxides stability, and supported by literature research.[27–29] It was found that all of the evaluated oxides were stable at the experiment parameters, with the exception of Cu_2O. The most stable oxide of copper is CuO, to which Cu_2O will eventually turn in normal atmosphere, especially when heated up.[27] This presents an interesting relation where the less stable oxide shows greater solubility, and is a potential field for further examination. In all other cases, the starting oxide and associated metal valence (Cu^{2+}, Mn^{3+}, Ni^{2+}, $Co^{2+/3+}$) remains stable during the thermal cycle. The starting oxide structure was confirmed through XRD (PANalytical Empyrean X-Ray diffractometer).

The measured concentrations of the metal oxides dissolved in the boron oxide (B_2O_3) glass at 900°C are listed in *Table 1*. The results indicate that the solubility in case of pure B_2O_3 is negligible. As presented by the X-EDS line analysis in *Fig. 3*, the metal content drops immediately after crossing the interface between the B_2O_3 glass and the pellet. Depending on the metal oxide used, the coloration of the samples varied according to the list shown in Table 1.

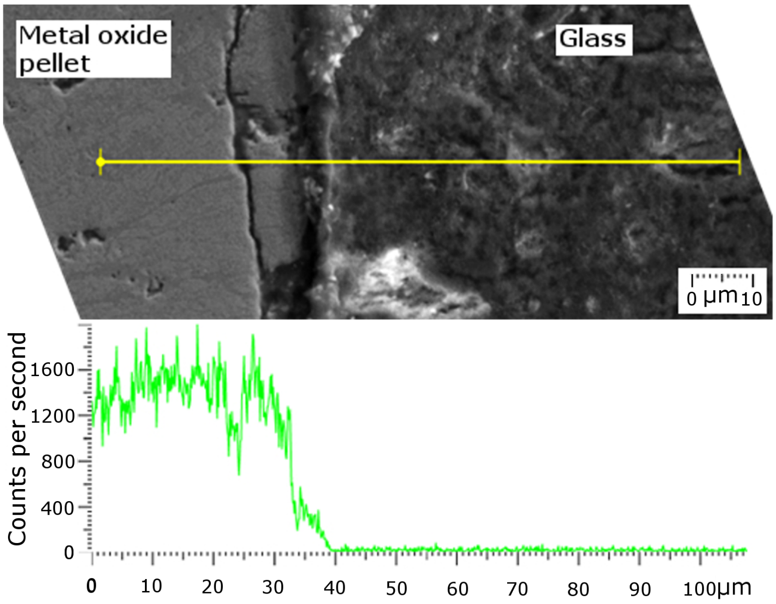


Fig. 3. A secondary electron image of nickel sample with X-EDS line scan

Table 1. Metal oxides solubility in B_2O_3 at 900 °C. The numbers present relevant metal species amount in the glass sample

Metal Oxide Formula	Metal Species Concentration (wt%)	Coloration
Co_3O_4	0.2	Pink
Cu_2O	0.6	Turquoise
CuO	0.3	Turquoise
Mn_2O_3	0.4	Colorless
NiO	0.5	Green

Low solubility, as indicated in Figure 3, can result from a *solubility gap* often present in similar systems, such as B_2O_3-FeO_x[30] however no high-concentration layer was observed around the pellets nor in any other regions. The only exception has been found in the case of Mn_2O_3. *Fig. 4* suggests existence of a high-concentration film on the interface in between the glass and metal oxide pellet, which could occur from the aforementioned solubility gap. The long equilibrating time introduced during the testing eliminates the possibility of the process kinetics limiting the solubility results, which means that the reason for the low values is of a thermodynamic nature.

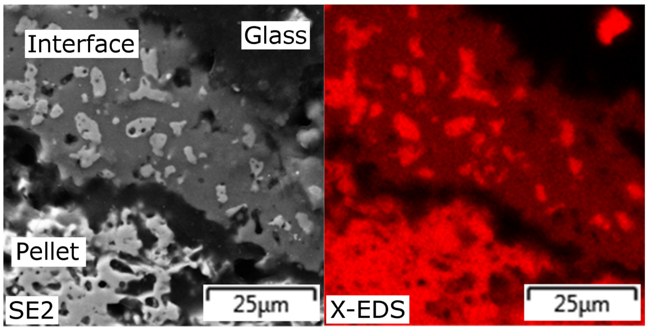
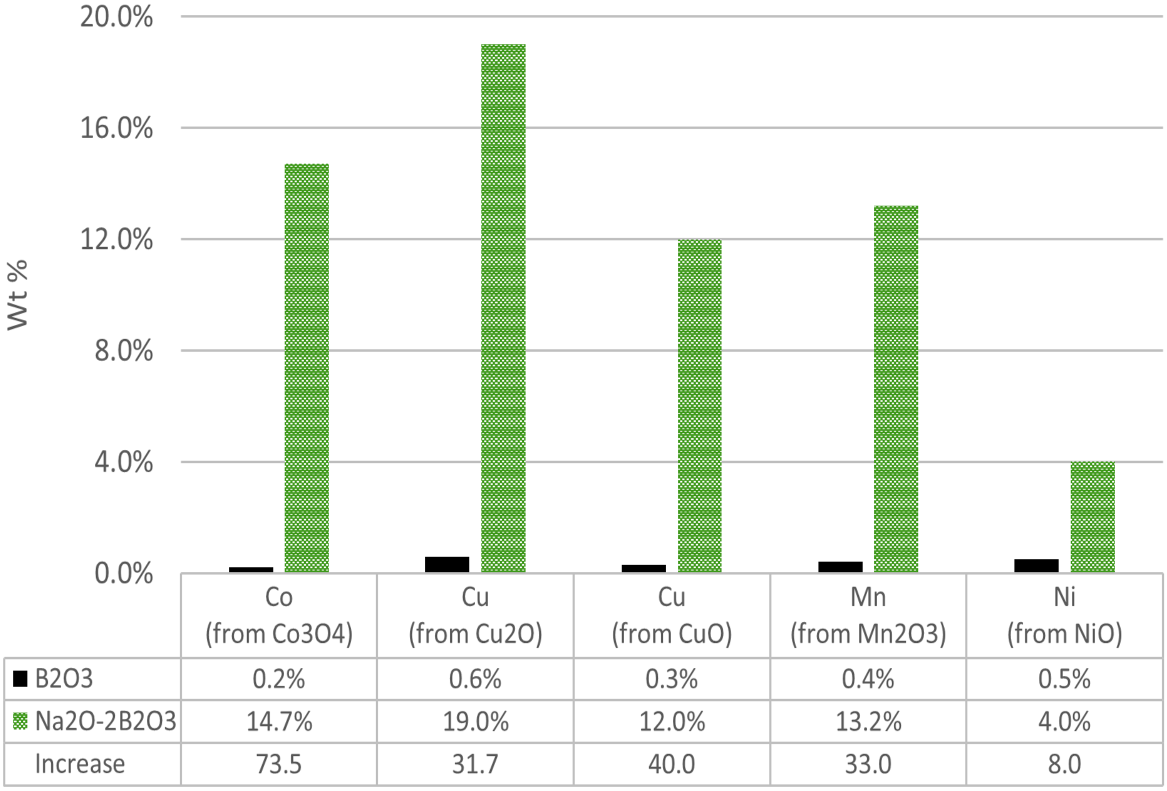


Fig. 4. SEM secondary electron image and X-EDS map of manganese content of Mn2O3-B2O3 interface

The impact of the sodium oxide presence in the glass (Na_2O-$2B_2O_3$) is shown in the *Fig. 5*, which shows the difference in solubilities of metal oxides between B_2O_3 and $Na_2B_4O_7$. The increase in solubility is substantial, from eight times in case of NiO up to more than seventy times for Co_3O_4. *Fig. 6* represents the uniformity of the metal distribution in the oxide phase, which indicates that the system has reached its equilibrium and the metal concentration is even throughout the bulk of the sample.



	Co (from Co3O4)	Cu (from Cu2O)	Cu (from CuO)	Mn (from Mn2O3)	Ni (from NiO)
■ B2O3	0.2%	0.6%	0.3%	0.4%	0.5%
▩ Na2O-2B2O3	14.7%	19.0%	12.0%	13.2%	4.0%
Increase	73.5	31.7	40.0	33.0	8.0

Fig. 5. The difference in metal oxide solubilities between the pure B_2O_3 and sodium oxide doped Na_2O-B_2O_3 at 900°C

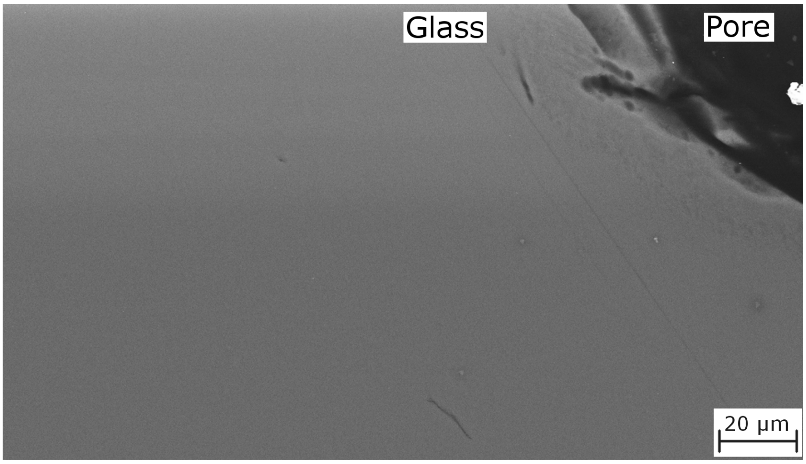


Fig. 6. Backscatter image of the Na_2O-2B_0O_3 + Cu_2O sample, showing the metal distribution uniformity

Interestingly, feeding less stable oxide of copper (Cu_2O) to the salt results in higher metal dissolution in the glass. From the thermodynamical point of view, Cu_2O oxidises further into CuO, although the kinetics of the process are slow have been reported to be slow.[27] This allows the cuprite pellet present in the crucible to remain partly as Cu_2O for some time during the dissolution process. If Cu^+ dissolves into the slag while also oxidising into CuO, then the final equilibration requires Cu^+ ion transport in the melt for oxidation to be complete. If this were to be slow, and Cu^+ had higher solubility compared to $Cu2^+$, this could explain the current results.

In an attempt to understand the reason behind the greater solubility of the Cu_2O over CuO, one can assume the Temkin[31, 32] model, in which molten salts are considered as completely ionised. This rules out the possibility of the overall ions concentration change in the solution, called the Ionic Strength, which is directly influencing different salts solubility in the water-based solutions. Limiting the miscibility is the positive enthalpy of mixing, which stays positive as long as the samples stay below their Upper Critical

Solution Temperature, as is true in our experiment.[31] The thermodynamics of mixing and the difference for these two copper oxides can theoretically be calculated, although the existing Temkin or Forland models treat the chemical species in the solution as pure components,[31] disregarding their oxidation state. Moreover, ideal models assume the zero enthalpy of mixing and random distribution of atoms.[33] Thus, the results of calculations based on the aforementioned models would be highly inaccurate. Guggenheim addressed the problem by creating quasi-chemical solution models,[33–35] which consider the non-random distribution of atoms and allow non-zero enthalpy of mixing. Such model could be built for the system in question, and derived in the attempt of describing the mixing parameters.

At this stage it remains speculative and further work is needed to explain the higher solubility observed with Cu2O compared to CuO. This would include identifying the oxidation state of Cu dissolved in the glass, which is nontrivial.

For the measurement of the solubility dependence on the temperature, the temperature of 1050°C was introduced to the sample containing Mn_2O_3 in the B_2O_3 melt. The solubility increase was negligible, showing that a temperature increase of 150°C was not significant enough to increase solubility and the slope of the phase diagram is very steep in this region. Future examination in this field is suggested to gain better understanding the influence temperature has on this salt set-up.

Another dopant for borate salt has also been experimented with. K_2O-$2B_2O_3$ has been heated up with a Mn_2O_3 pellet, following the same experiment procedure as the rest of samples. However, unlike Na_2O, K_2O showed little impact on the metal oxide solubility in B_2O_3, bringing only a negligible change to the concentration values. The nature behind this difference between Na_2O and K_2O remains unknown. In order to develop a deeper understanding and more complete picture of the phase formation and metal solubility behaviour for the borate salts, further testing needs to be done, with other metal oxide dopants.

IV. Conclusions

The limiting solubility of the following metal oxides: Cu_2O, CuO, Co_3O_4, Mn_2O_3 and NiO in borate glass has been measured, and the influence of a temperature change and other alkali metal oxides (Na_2O and K_2O) presence has been studied, filling the gap in the available experimental data. It has been concluded that pure B_2O_3 shows very limited solubility of the tested metal oxides, with the achieved concentration values below 1 wt%. The addition of Na_2O increased the solubility significantly, ranging from 8 times for NiO to over 73 times for Co_3O_4. K_2O-containing B_2O_3 salt has been investigated under the same conditions, yet it failed to show similar behaviour. The temperature increase from $900^{O}C$ to $1050^{O}C$ was not enough to make any significant change in the solubility of Mn_2O_3 in pure B_2O_3. Further investigation is necessary in order to understand the phase behaviour and create a more complete picture of the phase diagrams for borate salt systems.

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