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Contributed Paper

## Adhesion of Borosilicate Glass and Fe-Ni-Co Alloy Joined by Direct Fusion

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### ABSTRACT

The oxide scale of an Fe-Ni-Co alloy formed by pre-oxidation with a reducing LPG/O<sub>2</sub> or oxyacetylene flame before direct fusion to a borosilicate glass was studied. It was found that the amount of the oxide scale increased as the pre-oxidation time increased. The oxide scale is iron oxides consisting of hematite and magnetite. An investigation of the Fe-Ni-Co alloy to the borosilicate glass joints revealed that the contact angle between the glass and the alloy was affected by the amount of the oxide scale on the alloy surface prior to joining. The thicker the oxide scale resulted in the better wetting of glass to the alloy. It was found from scanning electron microscopy that the oxide scale dissolved into the glass. In the case that there is an excessive amount of the oxide scale prior to joining, fayalite was also observed to crystallise within the glass. This led to a negative effect on the strength of the joints. Transmission electron microscopy revealed a dispersion of fine fayalite and iron silicon carbonyl particles within the iron-rich zone where the oxide scale dissolved into the glass. The optimum condition for joining the borosilicate glass to the Fe-Ni-Co alloy is to preoxidise the alloy with a reducing flame for 2 minutes getting the weight gain of 0.59-0.83 mg/cm<sup>2</sup> prior to direct fusion. The bonding strength obtained was about 4 N/mm<sup>2</sup> (MPa).

**Keywords :** adhesion, borosilicate glass, direct fusion, Fe-Ni-Co alloy, joining.

### 1. INTRODUCTION

The Fe-Ni-Co alloy to borosilicate glass seals have been used for many years as hermetic and electrically insulating seals. It is not only excellent in thermal expansion matching but also in good wettability and bond strength too [1]. It was well known that the thermal expansion coefficient of the metal needs to be as close as possible to the glass and the oxide layer should be developed on the metal surface before sealing [2]. These mean the strong glass-metal adhesion requires

a continuous transition from the metallic structure of the metal, gradually, to ionic covalent structure of the glass [2,3].

Despite mechanism of adhesion in the Fe-Ni-Co alloy to borosilicate glass seals was studied by many investigators [e.g. 4-8], not much information on electron microscopy study has been reported. It is the purpose of this work to study the interface phenomena of the borosilicate glass and the Fe-Ni-Co alloy joined by direct fusion with emphasis on scanning and transmission electron microscopy.

## 2. MATERIALS

### 2.1 Fe-Ni-Co Alloy

The Fe-Ni-Co alloy used in this experiment was made by sintering of high purity metal powders in a nitrogen gas atmosphere. The metal powders were mixed with a composition of 54 wt%Fe, 29 wt%Ni and 17 wt%Co. The powder mixture of 10 g was uniaxially pressed at a load of 30 tons/in<sup>2</sup> to be disc-shaped specimens with a diameter of 1 inch. The green specimens were then pre-sintered at 950 °C for 2 hours in a nitrogen gas atmosphere followed by furnace cooling. The pre-sintered specimens were then re-pressed at a load of 50 tons/in<sup>2</sup> and sintered at 1,050 °C for 2 hours in a nitrogen gas atmosphere followed by water quenching.

### 2.2 Borosilicate Glass

A mixture of cristobalite 46.56wt%, alumina 1.33wt%, borax 46.97wt% and potassium carbonate 5.14wt%, was prepared by ball milling. The mixture was then transferred to an alumina crucible and melted in a gas furnace at 1400 °C for 4 hours. The glass obtained was poured into a hot metal mould forming a cylindrical rod with a diameter of 1 cm. The glass rod was consequently annealed in a gas furnace at 550 °C followed by furnace cooling to room temperature.

## 3. METHODS

### 3.1 Surface Cleaning

Specimens need to be cleaned before joining to eliminate organic substances on their surfaces. For the borosilicate glass, this was done by immersing in 10 vol% hydrosulfuric

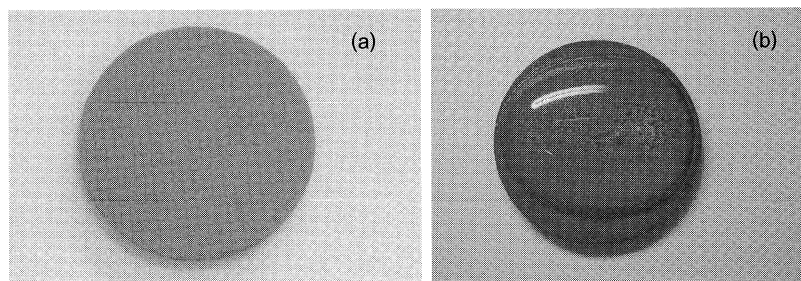
solution. For the Fe-Ni-Co alloy, cleaning was done by immersing the alloy in distilled water with 5 vol% hydrogen peroxide addition and heated to the boiling point for 30 minutes. After immersion, the specimens were rinsed with distilled water and methanol, dried and kept in a dessicator.

### 3.2 Preoxidation of the Alloy Surface Before Joining

Preoxidation of the Fe-Ni-Co alloy surface before joining was done by a reducing flame from a gas burner. Two types of fuels, i.e. acetylene and liquidfied petroleum gas (LPG), were used with oxygen gas as an oxidant. Preoxidation time in this experiment was in a range of 1-3 minute(s). The degree of oxidation was measured by weight gain of the specimens.

### 3.3 Glass-to-Metal Joining

The glass rod was cut into pieces of about 1.5 cm in length with the weight of 1.50 g. The glass piece was put on the alloy specimen. They were then joined by direct fusion using an oxidising flame from a gas burner. Again, two different fuels were used to compare the results, i.e. acetylene and LPG, with oxygen gas as an oxidant. Direct fusion was performed for 3 minutes during which the glass piece was melt and wet onto the alloy specimen. The joint was consequently transferred to an electrical furnace and annealed at 550 °C for 30 minutes followed by furnace cooling. Figure 1 shows the alloy specimen after preoxidation and after joining to the borosilicate glass by direct fusion.



**Figure 1.** An alloy specimen after preoxidation (a) and after joining to the borosilicate glass by direct fusion (b).

### 3.4 Characterisations

Hot mounting of the joints was done using phenolic resin and cross sections from the mounts were used in measuring the contact angle between the glass and the alloy by an Olympus BX60M light microscope. Crystal structures and chemical compositions of the Fe-Ni-Co alloy, the products formed by preoxidation of the alloy surface, and also phases at the interface of the joint were identified by x-ray diffractometry (XRD) using a Bruker AXS D8 Advance x-ray diffractometer and scanning electron microscopy - energy dispersive x-ray spectrometry (SEM-EDS) using a JEOL JSM-6335F scanning electron microscope operated at 15-20 kV. Thin specimens for transmission electron microscopy (TEM) were prepared by a double-jet polisher until a small hole was produced in the alloy, followed by ion beam thinning to enhance the hole into the glass area. A JEOL JEM-2010 scanning-transmission electron microscope was used and operated at 200 kV.

### 3.5 Strength of the Joint

Cross sections of the joint mounted in phenolic resin were used to evaluate the strength of the joint. They were put in a

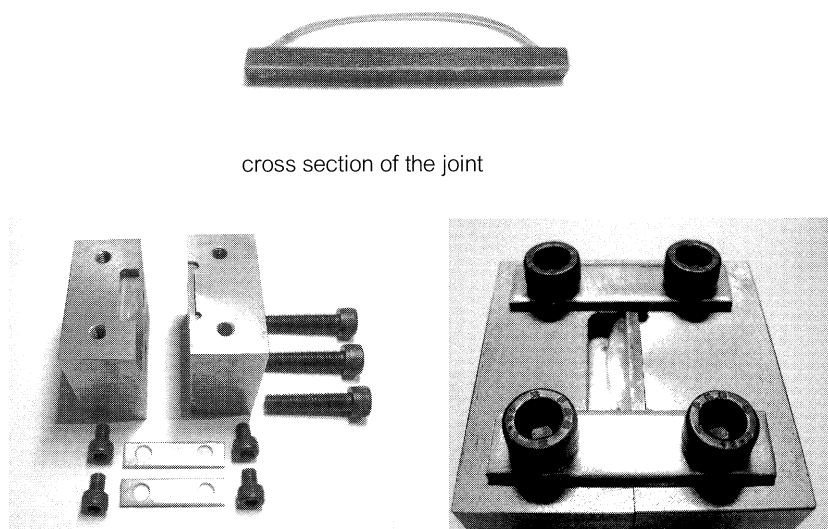
specially-designed holder (Figure 2) where a head load could be pressed only on the glass area and the alloy part was supported underneath by the holder. Compression testing was performed using a Hounsfield H10K universal testing machine.

## 4. RESULTS AND DISCUSSION

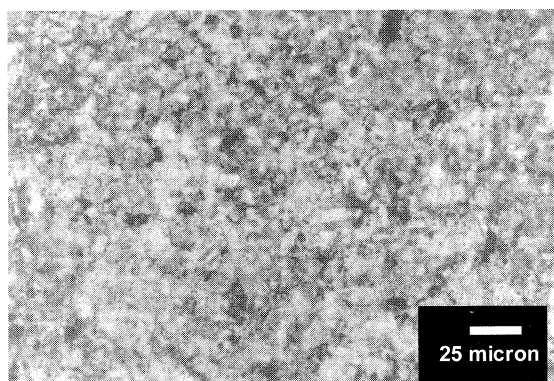
### 4.1 Microstructure of the Fe-Ni-Co Alloy

Figure 3 shows a typical microstructure of the Fe-Ni-Co alloy prepared in this experiment. X-ray diffractogram from the alloy was marked as sintered in Figure 4. Constituents of the alloy microstructure included taenite-like ( $\text{Fe}_3\text{Ni}_3\text{Co}$ ) and awaruite-like  $[\text{Fe}(\text{Ni}_{1-x}\text{Co}_x)_3]$  phases containing cobalt and also magnetite ( $\text{Fe}_3\text{O}_4$ ). A peak shift of awaruite at  $2\theta = 44.276^\circ$  was believed to be due to an existence of Co in the lattice. A broad peak at  $2\theta = 20-25^\circ$  was from the amorphous resin holder.

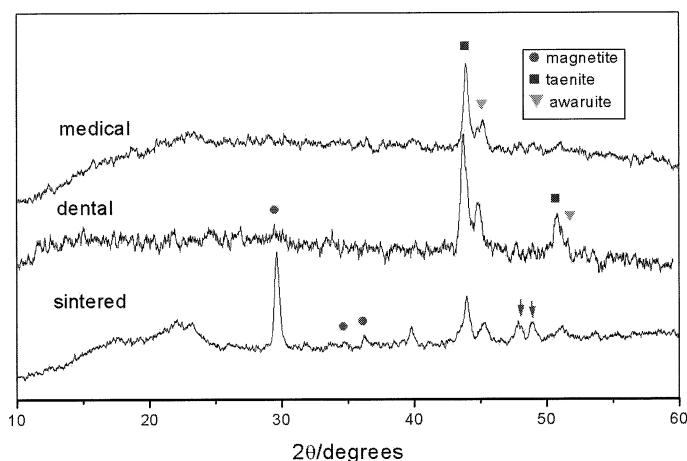
A backscattered electron image and energy dispersive x-ray spectrums of the alloy were given in Figure 5. The results confirmed an existence of  $\text{Fe}_3\text{O}_4$  as the dark phase, containing Fe and O, impinged within the light phases of taenite and awaruite, containing Fe, Ni and Co. The presence of iron oxide in the alloy suggests that iron powder was partially



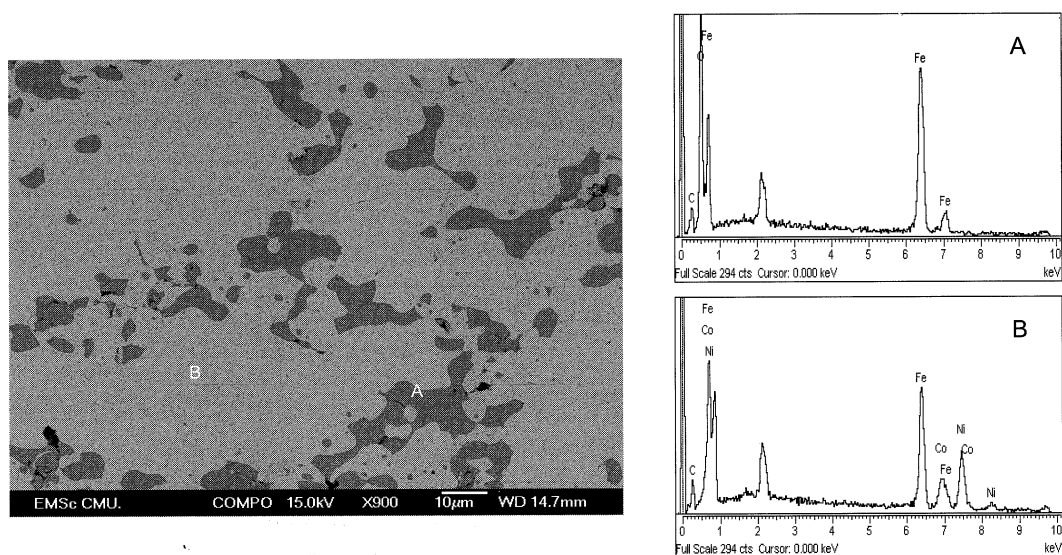
**Figure 2.** A cross section of the joint and the holder for testing strength of the joint.



**Figure 3.** A typical microstructure of the Fe-Ni-Co alloy prepared in this experiment.



**Figure 4.** X-ray diffractogram from the Fe-Ni-Co alloy prepared in this experiment compared to the commercial alloys used in the dental and medical x-ray tubes.



**Figure 5.** A backscattered electron image and energy dispersive x-ray spectrums of the Fe-Ni-Co alloy. The magnetite is marked A, while the area of taenite-like and awaruite-like phases containing cobalt is marked B.

oxidised during sintering.

#### 4.2 Weight Gain and Products on Surface of the Preoxidised Alloy

Figure 6 shows cross sections of the alloy preoxidised by reducing LPG/O<sub>2</sub> and C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub> flames, respectively. The thickness of the oxide scale layer in both cases was in the range of 40-160 microns whereas weight gain by oxidation was in the range of  $1.614 \times 10^{-4}$  -  $14.93 \times 10^{-4}$  g/cm<sup>2</sup>, as shown in Figure 7, increased as the preoxidation time increased. The porosity in the oxide layer and the rate of oxidation were greater when the oxyacetylene flame was used due to the higher temperature of the flame. This is in agreement with the results reported by Mantel [2] and Pask [4]. The percentage of porosity in the oxide layer measured by point counting was about 20vol% and 51vol% in the case of LPG/O<sub>2</sub> flame and C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub> flame, respectively. Intergranular oxide formed at grain boundaries was also observed as reported by Yext et al. [5].

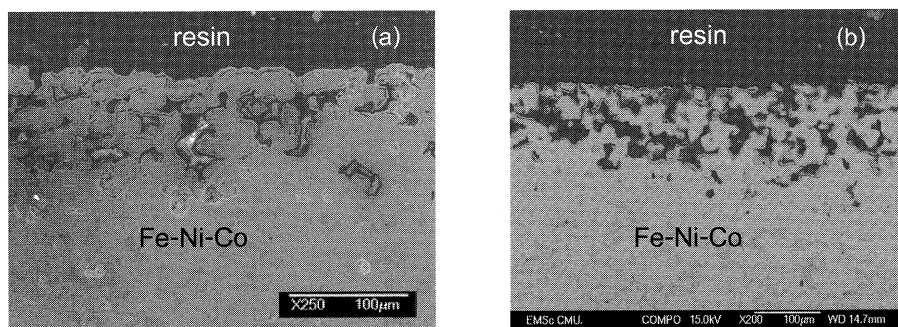
X-ray diffractograms of the preoxidised surface at different preoxidation time were given in Figure 8. The results suggest that the oxide scale consists of hematite (Fe<sub>2</sub>O<sub>3</sub>) and magnetite (Fe<sub>3</sub>O<sub>4</sub>). The relative amount of hematite was increased as the preoxidation time increased. This is in agreement with Zanchetta et al. [6]. Peaks from the bulk alloy were also observed as taenite and awaruite as already mentioned in Figure 4.

X-ray line scanning at cross section of the preoxidised alloy was shown in Figure 9. It can be seen that there is an area underneath the outer iron oxide layer where the Fe content drastically decreased as the amount of Ni and Co was increased. This is in agreement with the previous investigations [6-8]. The reduction of the iron content in such area was believed to be due to selective oxidation of iron leading to a complex structure including magnetite and an alloy riched in Co and Ni.

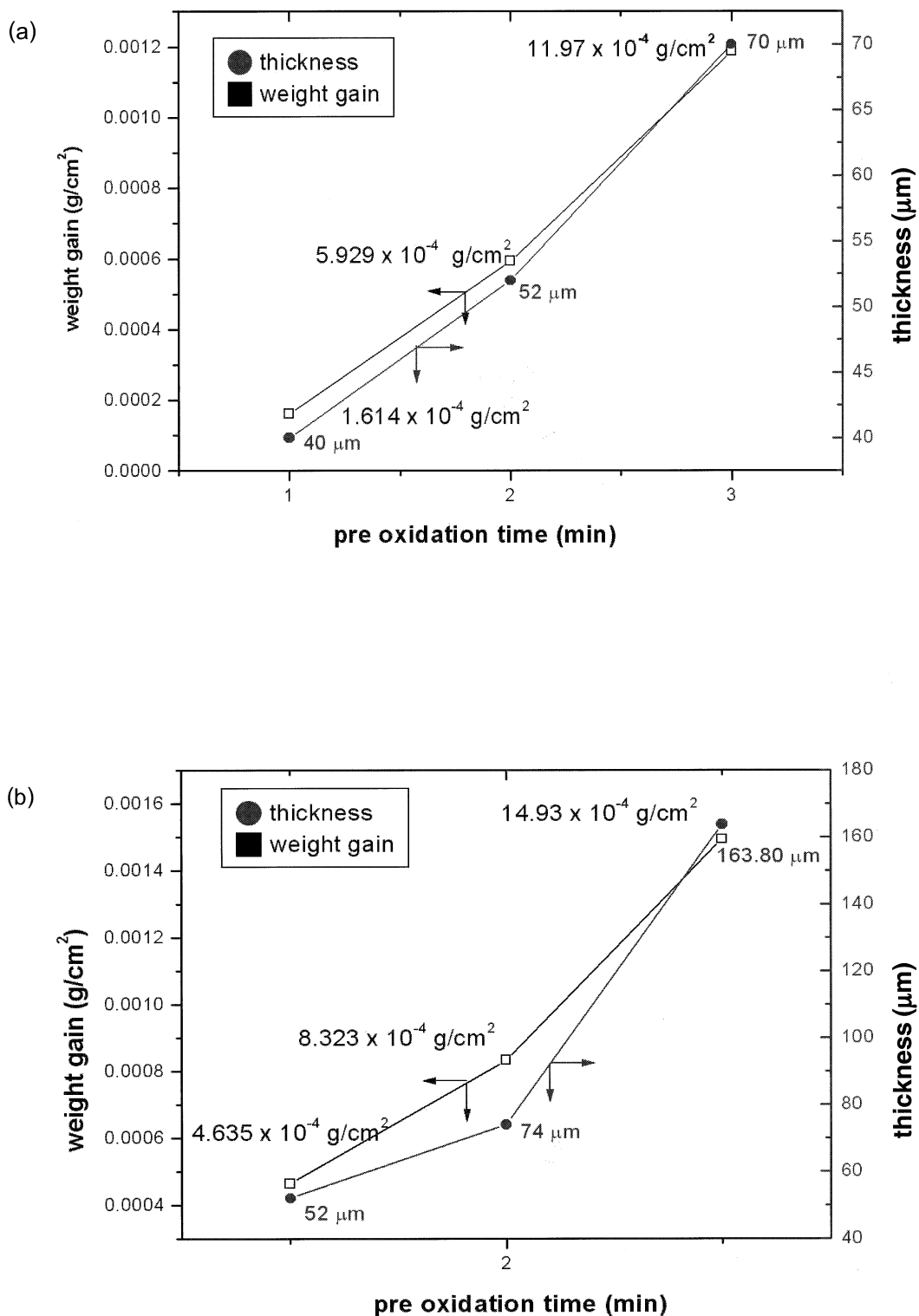
#### 4.3 Contact Angle and Interfacial Phenomena of the Joint

Contact angle between the borosilicate glass and the Fe-Ni-Co alloy was measured from cross sections. The average value was in the range of 45° - 36° decreasing as the thickness of the oxide scale increased (Figure 10). Therefore, wetting of the glass to the alloy was improved by the presence of the oxide scale on the alloy surface. This could be attributed to the change in the surface tension and also the porosity in the oxide layer helping dispersion of the glass.

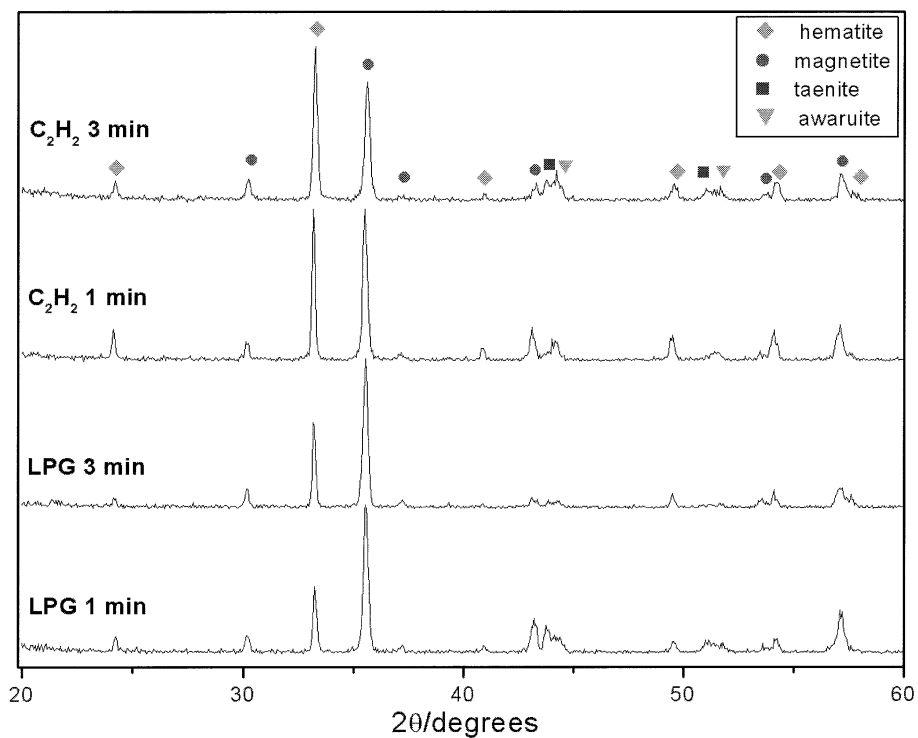
An investigation on cross sections of the joints by backscattered electron imaging and x-ray line scanning revealed that the oxide scale, formed by preoxidation with the time less than 2 minutes, mostly dissolved into the borosilicate glass after direct fusion joining. This led to a Fe-riched area as an interlayer at the interface (Figure 11). On the other hand, the amount of the oxide scale formed by



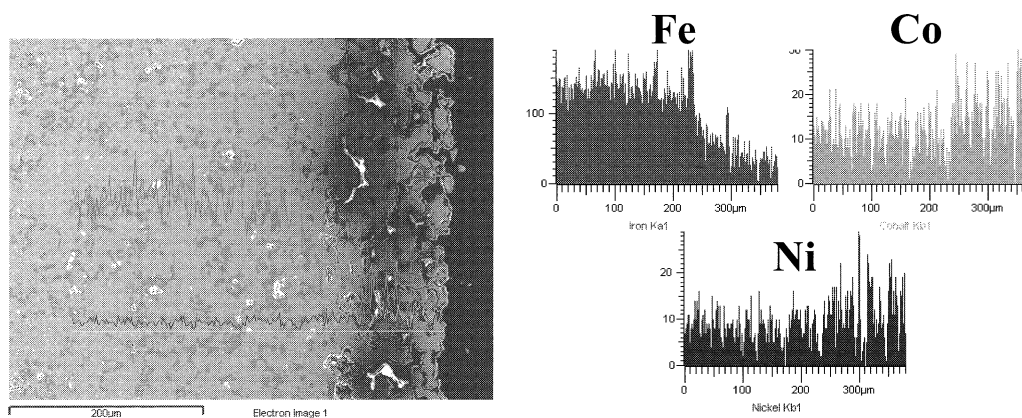
**Figure 6.** Cross sections of the alloy preoxidised by reducing LPG/O<sub>2</sub> flame (a) and C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub> flame (b).



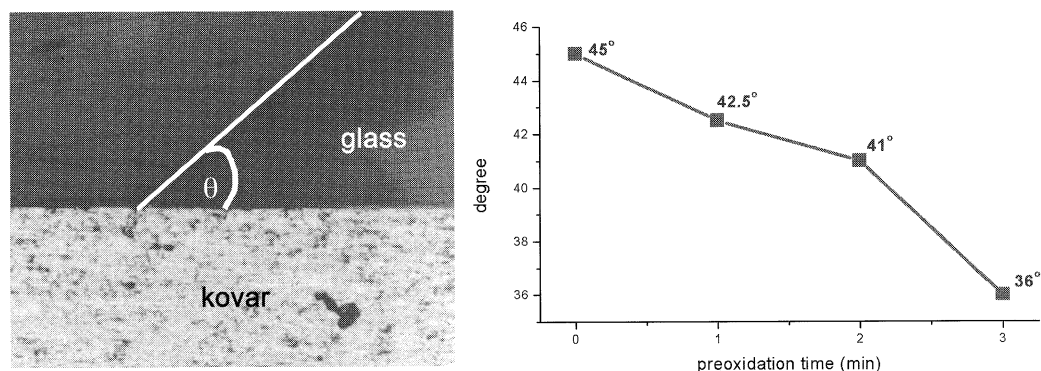
**Figure 7.** Thickness and weight gain of the alloy preoxidised by reducing LPG/ $\text{O}_2$  flame (a) and  $\text{C}_2\text{H}_2/\text{O}_2$  flame (b).



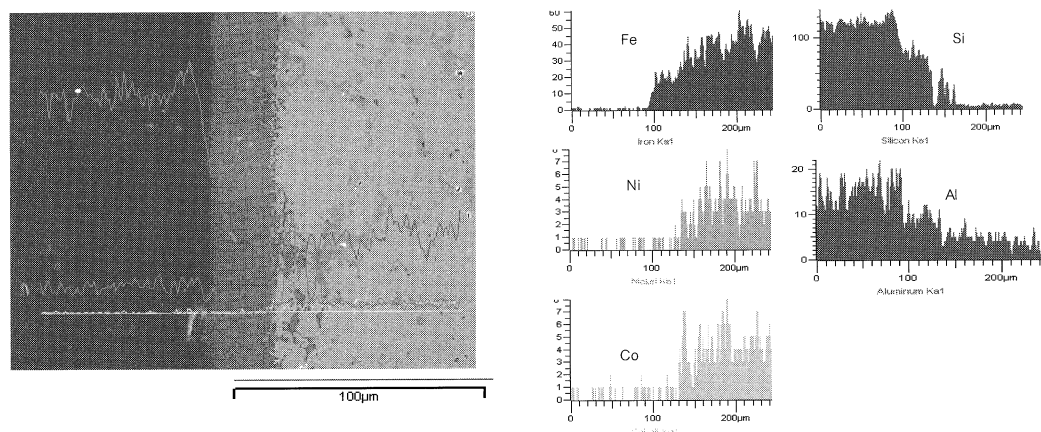
**Figure 8.** X-ray diffractograms of the preoxidised surface of the Fe-Ni-Co alloy.



**Figure 9.** X-ray line scanning at a cross section of the alloy preoxidised by reducing LPG/ $O_2$  flame.



**Figure 10.** Contact angle between the borosilicate glass and the Fe-Ni-Co alloy without and with preoxidation at various times.



**Figure 11.** Backscattered electron image and x-ray line scanning of the joint. (preoxidation with LPG/O<sub>2</sub> for 2 minutes).

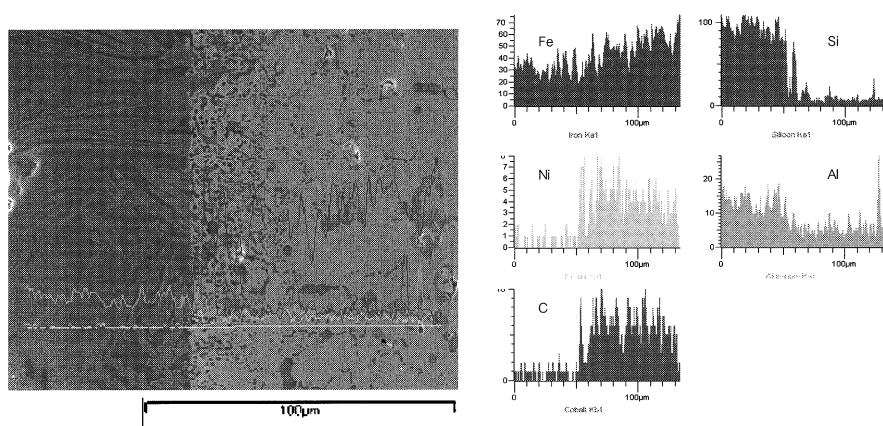
preoxidation for 3 minutes was excessive and partially dissolved into the borosilicate glass leading to devitrification within the glass at the vicinity closed to the interface (Figure 12). The results from energy dispersive x-ray microanalysis (Figure 13) and x-ray diffractometry (Figure 14) confirmed that the devitrified dendritic crystals were fayalite (Fe<sub>2</sub>SiO<sub>4</sub>). Comparison between the cases of LPG/O<sub>2</sub> and C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub> flames, there is not much difference in microstructure apart from that the thicker Fe-rich interlayer or fayalite-crystallised area was found in the latter case, because of diffusional enhancement by higher flame temperature. Penetration of the glass into the porosity of the alloy at the interface was also observed. The results were in agreement with Zanchetta et al. [6] and Ikeda

and Sameshima [7]. In the case where the joining was performed without preoxidation of the alloy surface, the interface was taken apart during cross sectioning. Therefore, it can be concluded that good adhesion is in association with a mechanical bonding of the glass penetrated into the porosity at the alloy surface together with a chemical bonding. An appropriate amount of the oxide scale formed by preoxidation of the alloy must be dissolved into the glass forming the Fe-rich interlayer without devitrification of large dendritic crystalline phase.

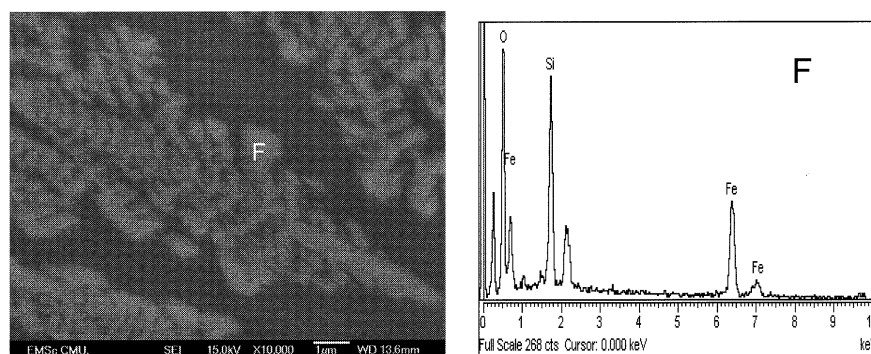
#### 4.4 Transmission Electron Microscopy Study

TEM investigation was performed on the Fe-rich interlayer, where the oxide scale

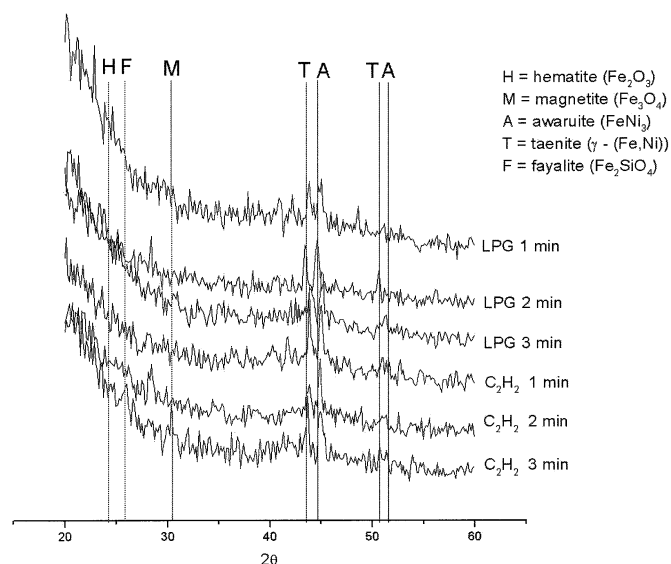




**Figure 12.** Backscattered electron image and x-ray line scanning of the joint. (preoxidation with  $C_2H_2/O_2$  for 3 minutes).



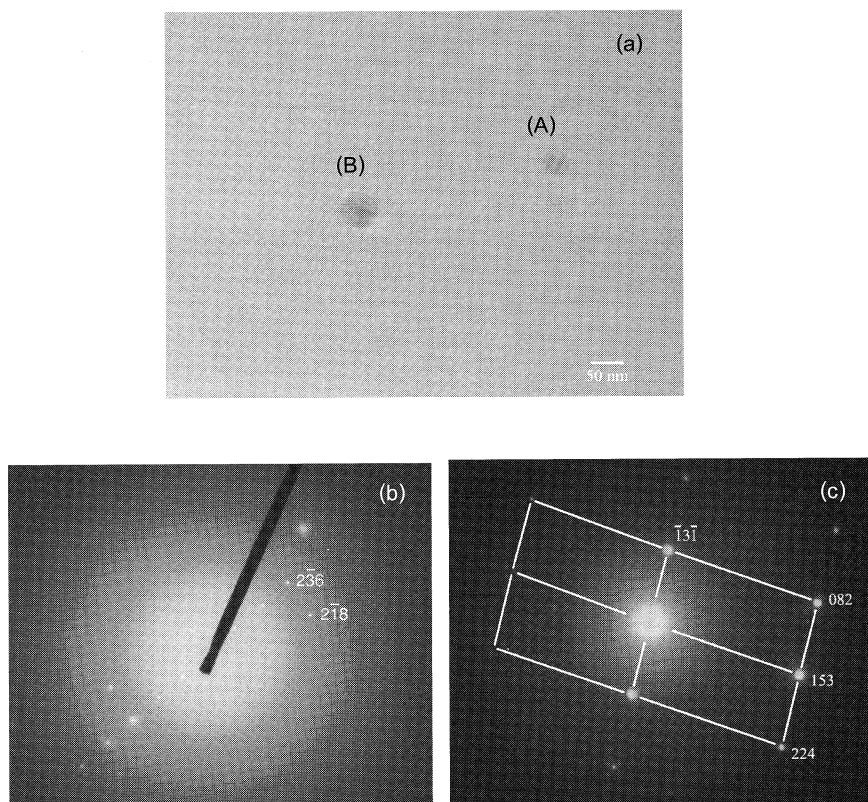
**Figure 13.** Energy dispersive x-ray microanalysis of devitrified dendritic fayalite (bright area marked F) in the glass closed to the interface of the joint. (preoxidation with  $C_2H_2/O_2$  for 3 minutes).



**Figure 14.** X-ray diffractograms showing the constituents found at the interface of the joint.

was dissolved into the glass as observed by SEM-EDS. The investigation revealed a dispersion of fine fayalite ( $\text{Fe}_2\text{SiO}_4$ ) and possibly also iron silicon carbonyl ( $\text{SiFe}_4(\text{CO})_{16}$ ) particles within glass near the interface of the

joint (Figure 15). This suggests that, even though large dendritic crystal is not observed in macroscale, devitrification can still take place as nanoscale crystalline particles within the Fe-rich zone in the glass.



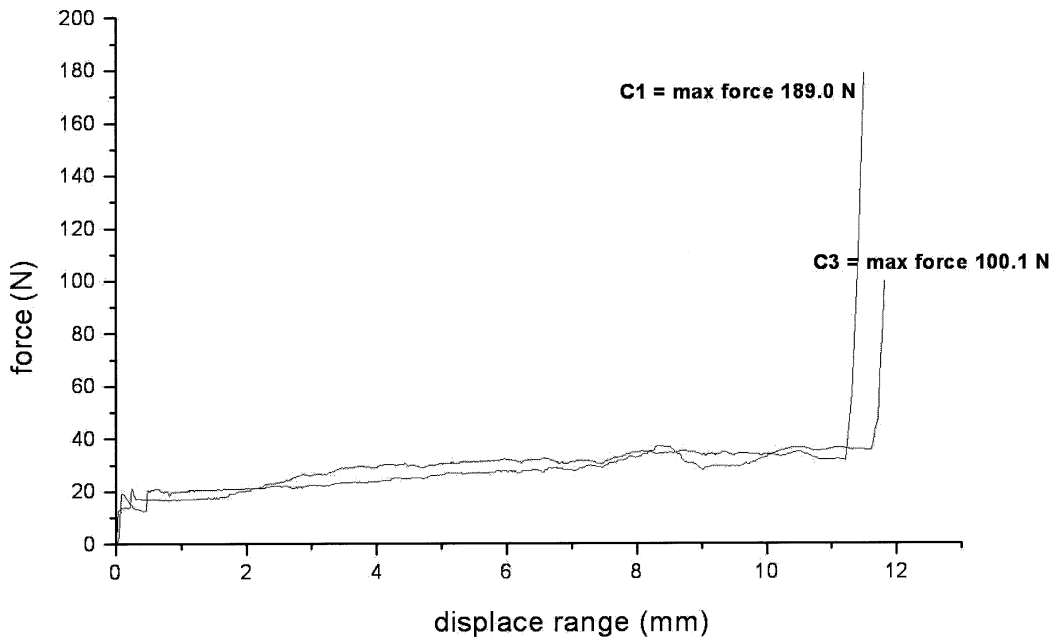
**Figure 15.** (a) A bright field TEM micrograph shows fine precipitates within the glass closed to the interface. (b) and (c) corresponding SADPs from particles marked A (iron silicon carbonyl) and marked B (fayalite), respectively.

#### 4.5 Strength of the Joint

The results from compression testing of the joints with and without devitrification of dendritic fayalite were given in Figure 16. The strength of the joint without devitrification of dendritic fayalite was about 4 N/mm<sup>2</sup> (MPa). This value is comparable to the result reported by Macey et al. [1], which was 4.5 N/mm<sup>2</sup>. In the case where no dendritic fayalite was crystallised, fracture occurred at the glass-metal interface, not in the glass close to the interface as observed in the opposite case. This suggests a negative effect of dendritic fayalite crystal on the strength of the joint.

#### 5. CONCLUSIONS

- (i) The outer surface products from preoxidation of the Fe-Ni-Co alloy consist of hematite ( $\text{Fe}_2\text{O}_3$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ). Underneath the outer layer, there exists a Fe-depleted layer with a complex structure including magnetite and an alloy riched in Co and Ni.
- (ii) Both SEM and XRD examinations confirmed that, at the preoxidation time more than 2 minutes in this experiment, the oxide scale formed by preoxidation was excessive and partially dissolved into the borosilicate glass leading to devitrification of dendritic iron silicate (fayalite).



**Figure 16.** The strength of the joint without (C1) and with (C3) devitrification.

- (iii) TEM investigation suggests that at the Fe-rich zone of the glass into which the oxide scale dissolved, nanoscale crystalline particles can exist, even though no large dendritic crystal is observed in macroscale.
- (iv) The optimum condition for joining the borosilicate glass to the Fe-Ni-Co alloy in this experiment is to preoxidise the alloy for 2 minutes getting the weight gain of 0.59-0.83 mg/cm<sup>2</sup>. Good adhesion is in association with a mechanical bonding of the glass penetrated into the alloy surface *via* porosity together with a chemical bonding. An appropriate amount of oxide scale formed by preoxidation of the alloy must dissolve into the glass forming a Fe-riched interlayer without devitrification of dendritic fayalite.
- (v) In the case of no devitrification of dendritic fayalite, fracture occurred at the glass-metal interface and the strength of the joint was about 4 N/mm<sup>2</sup> (MPa).

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