Formation of Hercynite ($FeAl_2O_4$) at Interface of Al_2O_3/Steel Joint†

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The joining of ceramics to metals has received considerable interest in recent years in connection with the high strength of ceramics. Major methods reported are refractory-metal metallizing, active alloy sealing, oxide-soldering and metal-oxide eutectic utilizing[1)-3)]. These methods, however, require the complicated process for joining. On the other hand, we scceeded in joining alumina to steel using copper-filler metal in a slightly oxidizing atmosphere. In this work, we will report the intermediary layer compound $FeAl_2O_4$ formed at a bonding interface between alumina and steel.

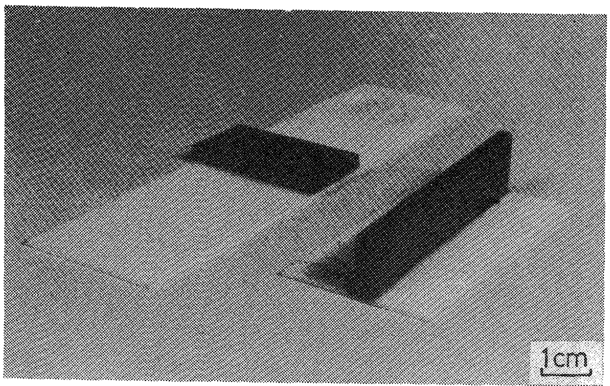

Fig. 1 Al_2O_3/Steel brazed samples with copper filler metal: (1) alumina butt joint strapped with steel, (2) alumina/steel tee joint.

The materials used were high purity commercial alumina (95.4%), mild steel (SS41) and copper foil of 0.12 mm in thickness. The joining has been conducted in 10 torr at 1200°C for 30 min. The liquid copper during joining wetted both alumina and steel at 1200°C, and hence a strong bond was formed after cooling down. Various types of joining were produced by using steel and copper filler metals. Alumina butt joint strapped with steel and alumina/steel tee joint are shown in **Fig. 1**.

In order to characterize the intermediary layer of

Table 1 X-ray diffraction analysis of alumina surface joined in 10 torr at 1200°C for 30 min.

number	d_{obs}. (Å)	Intensity		α-Al_2O_3 in ASTM card			$FeAl_2O_4$ in ASTM card		
				d(Å)	(hkl)	I/I_1	d(Å)	(hkl)	I/I_1
1	A 3.440	84		3.479	(012)	75			60
2	2.849		58				2.87	(220)	
3	A 2.529	76		2.552	(104)	90			
4	2.436		100				2.45	(311)	100
5	A 2.362	60		2.379	(110)	40			
6	2.071	100		2.085	(113)	100			
7	2.023		40				2.02	(400)	80
8	A 1.731	49		1.740	(024)	45			
9	1.656		34				1.64	(422)	16
10	A 1.593	68		1.601	(116)	80			
11	1.558		57				1.56	(511)	40
12	1.435		54				1.43	(440)	80
13	A 1.400	42		1.404	(124)	30			
14	A 1.370	68		1.374	(030)	50			

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joint, steel and copper were dissolved from the alumina/steel joint in concentrated hot HNO_3 solution, and X-ray diffraction analysis with $Cu \cdot K_\alpha$ radiation and X-ray photo-electron spectroscopic examination with $Mg \cdot K_\alpha$ excitation were conducted to identify the intermediary compound. X-ray diffraction analysis demonstrates the formation of hercynite ($FeAl_2O_4$) at interface between copper and α-alumina as shown in **Table 1**. The X-ray reflections were assigned to alumina with rohmbohedral structure and hercynite with cubic structure (a=8.119Å).

The formation of intermediary compound is also known in another system[3]: $CuAlO_2$ has been found between copper oxide and alumina after reaction at 1150°C in air. In the refractory metal-joining process (moly-manganese), manganese oxide reacts with alumina and forms the intermediary compound $MnO \cdot Al_2O_3$.

Further examination of the intermediary layer compound was carried out by X-ray photoelectron spectrometry. The C1s spectrum (285.00 eV) from the contaminant carbon was used for the calibration of binding energies of electrons. The $Fe2p_{3/2}$, A12p and O1s electron spectra are given in **Figs. 2-4**, respectively.

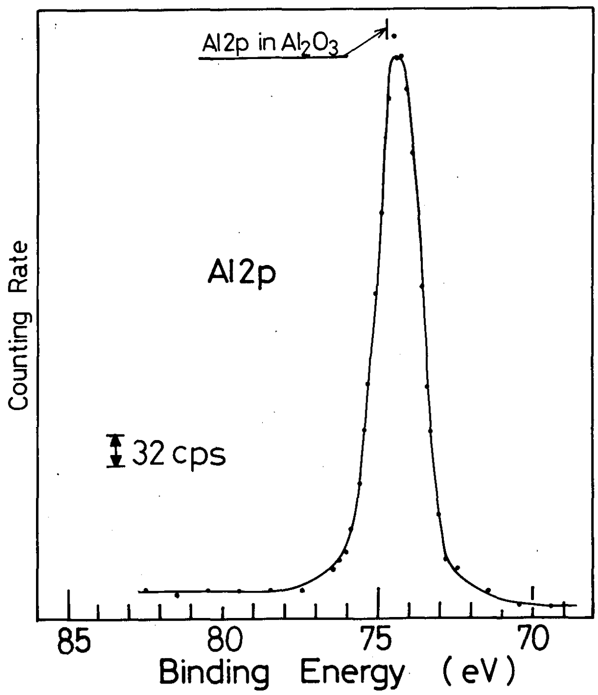

Fig. 3 Al2p spectrum of the revealed surface on alumina, after dissolution of steel and copper from a alumina/steel joint with copper filler.

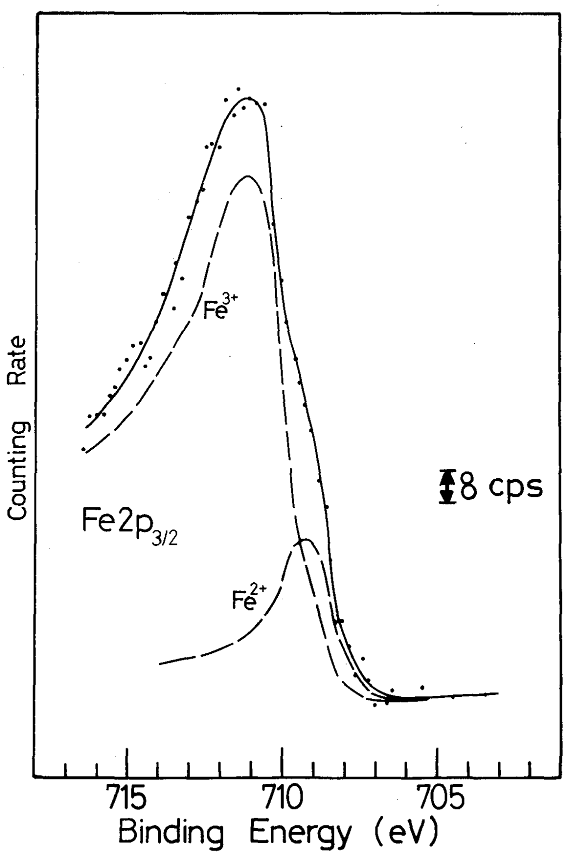

Fig. 2 $Fe2p_{3/2}$ spectrum of revealed surface on alumina, after dissolution of steel and copper from a alumina/steel joint with copper filler.

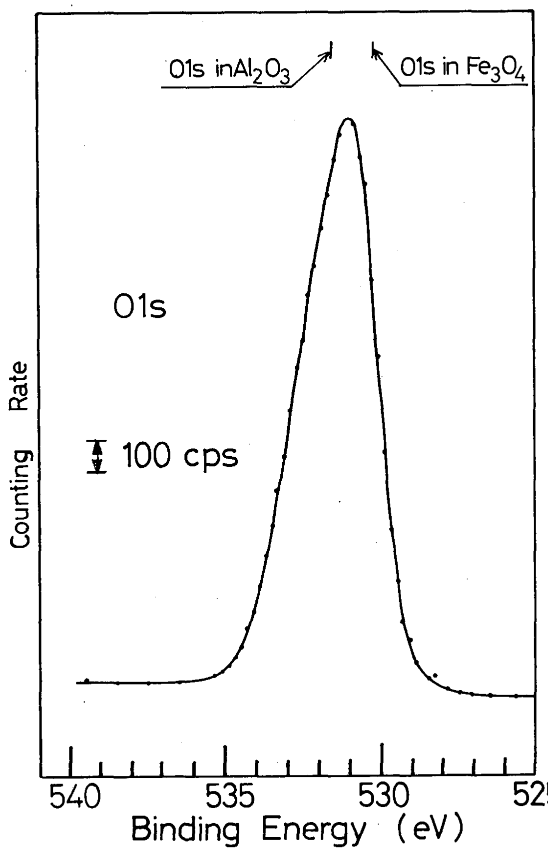

Fig. 4 Ols spectrum of the revealed surface on alumina, after dissolution of steel and copper from a alumina/steel joint with copper filler.

The $Fe2p_{3/2}$ consists of superposed spectra originating from Fe(III) and Fe(II) components[4]. The binding energies of the Fe2p electrons are taken as 711.20 and 709.20 eV for Fe(III) and Fe(II), respectively. The spectrum of Fe(II) can be attributed to hercynite ($FeAl_2O_4$). The intense spectrum of Fe(III) suggests that the surface of $FeAl_2O_4$ has been oxidized during specimen preparation, particularly, during boiling in hot concentrated HNO_3. The binding energy of A12p (74.35 eV) measured is very close to that for Al_2O_3 (74.70 eV). The binding energy of the O1s electrons (531.00 eV) is different from those of Al_2O_3 (531.55 eV) and Fe_3O_4 (530.17 eV), since the binding energy of O1s electrons changes with coexisting cations in the specimen[5].

It can, therefore, be concluded that the intermediary layer compound $FeAl_2O_4$ is formed between Al_2O_3 and steel during joining using copper-filler with a consequent strong adhesion.

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