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Reaction and Interfacial Characterization on Joining of Zirconia to Carbon Steel[†]

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Abstract

Reaction between zirconia and carbon steel was studied in the vacuum condition and interfacial characterization was performed using various spectroscopic methods such as TFXD, ESR, and XPS. It is indicated from TFXD result that magnetite phase was detected at the interface as a result of reacting metallic iron with zirconia and weak interface between magnetite and metallic iron produced no good strength of joint. ESR result shows that small amount of iron diffused into zirconia lattice in the form of trivalent ion which causes ESR absorption near $g = 2.06$. The formation of trivalent zirconium ions in the interface was also supported by the appearance of ESR absorption at $g = 1.944$ with decreasing temperature, which is a proof of redox reaction between zirconia and metallic iron. Chemical state of iron clarified by XPS and appearance of broad ESR absorption due to Fe^{3+} - Fe^{3+} interaction shows a good agreement with TFXD result.

KEY WORDS: (Zirconia) (Characterization) (TFXD) (SIMS) (ESR) (XPS)

1. Introduction

Much attention has recently been paid to zirconia ceramics as one of the high functional materials, after developing the highly toughened zirconia¹⁾ and the thin film zirconia²⁾ et al.. In the case of using ceramics as structural materials, however, there has been still unsolved many problems on thermal and mechanical properties such as fractural toughness and creep. Many investigations regarding the ceramic/metal joining have been carried out. It has been succeeded to join zirconia to metals such as copper³⁾, nickel³⁾ and platinum^{4,5)}.

Steel is one of the most widely used and lowest cost metal. Until now, high strength joint of steel to zirconia without any insert materials has not been obtained. Purpose of the investigation is to characterize the chemical state of the interface between carbon steel and zirconia after solid state reaction by various spectroscopic methods. This study is expected to be the basic study for making carbon steel high functional by joining to zirconia.

2. Experimental Procedure

A sintered zirconia (3 mol% Y_2O_3 stabilized, 1723 K sintered, Osaka Cement Co.) and carbon steel (SM50A, < 0.2 wt% carbon) were used. Square zirconia plates with 9 × 9 mm and 3 mm in thickness and square carbon steel plates with 9 × 9 mm and 4 mm in thickness were used.

Zirconia plates were ground using a #325 diamond

wheel and carbon steel plates were polished with a #1500 emery paper. After grinding and polishing, the specimens were washed in acetone using ultrasonic waves.

After drying well, a zirconia plate was put between carbon steel plates, and then the solid state reaction was carried out by heating at 1273 K for 3.6 ks under the vacuum condition (10^{-2} – 10^{-3} Pa). About 100 kPa pres-

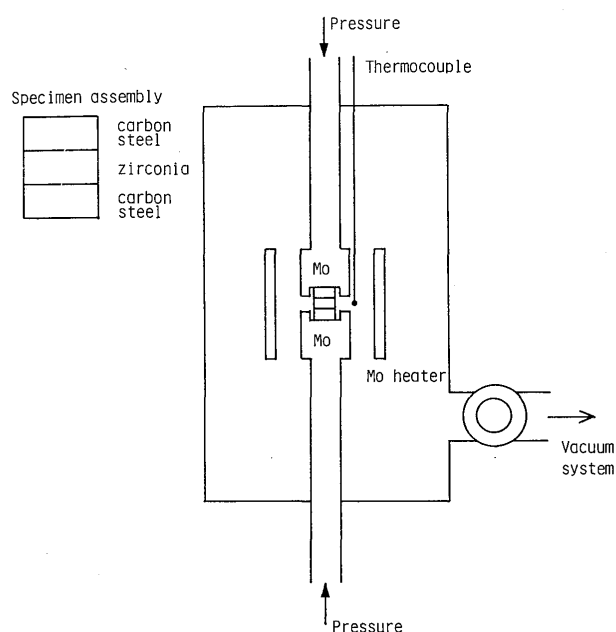


Fig. 1 Experimental apparatus for joining zirconia to carbon steel.

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sure was applied to the specimen assembly. The experimental apparatus is shown in Fig. 1.

In order to characterize the reacted region between zirconia and carbon steel, SEM observation, EDX, XRD, SIMS, ESR and XPS analyses were performed.

SEM observation was performed using a microscope of HSM-2B type (Hitachi Co.), operating at 20 kV and 100 μ A.

X-ray diffraction pattern was measured with Cu K α radiation using the diffractometer (Rigaku Co./Thin Film X-ray Diffraction system (TFD system)) for surface region analysis of zirconia. Diffractometer was operated at 50 kV and 200 mA.

Iron in the zirconia was examined by SIMS using Ar⁺ ion beam. A Hitachi IMA-SS spectrometer was used and operated at 10 kV below the vacuum condition of 1×10^{-4} Pa.

ESR spectra were measured with X-band method using a spectrometer of E-109 type (Varian Co.). Magnetic field available was 1 tesla (T), modulation frequency and field were 100 kHz and 1 mT respectively.

X-ray photoelectron spectra of zirconia surface were measured using ESCA Lab-5 system (VG Scientific Co.) under a vacuum of 1×10^{-7} Pa or higher. Sputtering of surface was performed using Ar⁺ ion beam and the rate was about 1 nm/min. Charging effect was corrected using C_{1s} peak position (284.6 eV) as standard one.

3. Results

Only weak joint was obtained. Scanning electron micrograph of the reacted region between zirconia and carbon steel is shown in Fig. 2. Dark region of about 15 μ m in thickness was observed in the zirconia near the interface. Zirconium and iron were detected from EDX analysis. Intensity of iron was very small as shown in Fig. 2.

TFXD pattern obtained from fractured surface of zirconia side of the joint is given in Fig. 3. Existence of tetragonal zirconia (t-ZrO₂) and magnetite (Fe₃O₄) phase were certified. Some peaks due to magnetite phases were not observed. Peak intensity showed some disagreement with standard value of ASTM card (card No. 19-629).

Secondary ion mass spectrum of iron, yttrium, and zirconium obtained from the fractured surface of zirconia side of the joint after sputtering for 100 min. is shown in Fig. 4. Comparing the intensity of zirconium, yttrium, the amount of iron on the fractured surface was very small. Secondary ion mass spectrum peaks of molecular ions of yttrium and zirconium (YO⁺ and ZrO⁺) were also observed.

ESR spectra of zirconia after fractured are shown in

Figs. 5 and 6. Broad and sharp absorptions are observed near 320 mT and these absorptions are overlapped with each other. The intensity of the sharp absorption is small and g-value was about 2.06. The spectrum depended on the direction of applied magnetic field and extra absorption appeared near 160 mT in the case of locating specimen zirconia so as to put the reacted surface parallel with magnetic field. With decreasing measured temperature, another sharp absorptions began to appear and was clearly observed at 123 K. The sharp absorption was observed at g = 1.944 and it was clearly distinguished with the small sharp absorption with g = 2.06 observed at room temperature.

X-ray photoelectron spectra of Zr_{3d}, Fe_{2p}, and O_{1s} are shown in Fig. 7 to 9. Compared with standard peak positions, remarkable chemical shifts were observed in the spectra of Zr_{3d} and O_{1s}. And the amount of these chemical shifts became smaller, with increasing sputtering time. On the other hand, Fe_{2p} peaks were observed after sputtering for 5 min whereas the peaks disappeared after sputtering for 30 min.

4. Discussion

Detection of small amount of iron in dark region of zirconia suggests that iron diffused into zirconia phase. However, sharp drops in constituent element profiles of EDX line analysis indicated the formation of very thin reaction layer between zirconia and carbon steel. Though black zirconia such as non-stoichiometric zirconia can be imagined from appearance of black region in the zirconia near the interface, conduction effect due to solid-solution of iron should be also considered in SEM observation.

Detection of tetragonal zirconia and magnetite phase on reacted zirconia by TFXD method indicates that magnetite was formed between zirconia and carbon steel and strength between magnetite and carbon steel (or wüstite phase) was weak. As far as surface layer of zirconia side was analyzed by TFXD method, solid-solution of iron and/or formation of magnetite phase on zirconia after reacting with carbon steel did not cause to transform from tetragonal zirconia to monoclinic zirconia. The result suggests no diffusion of yttrium to magnetite phase. The suggestion shows somewhat in consistent with SIMS result. Intensity of iron is very small than those of yttrium and zirconium, even if difference between sputter yields of these elements is taken into consideration.

According to previous papers^{6,7,8}, Fe³⁺, Zr³⁺, Y²⁺ ions can arise ESR absorptions, respectively. Absorptions relating to Fe³⁺ ions can be very often observed in crystal line and amorphous solids, and it is most reasonable to assign the broad absorption to Fe³⁺ ions in the

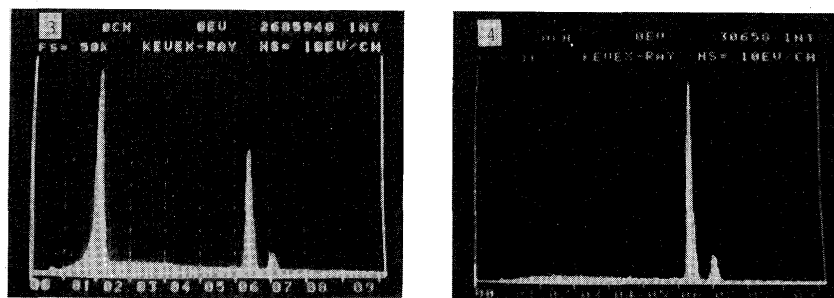
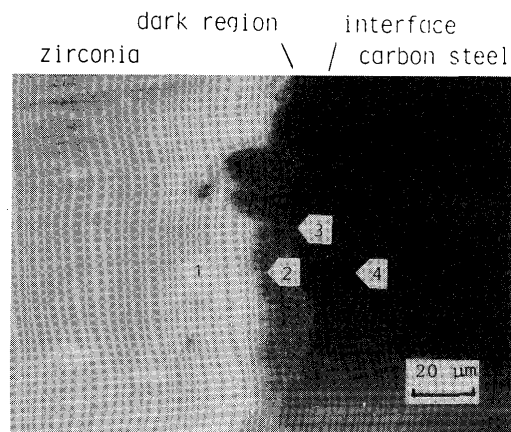
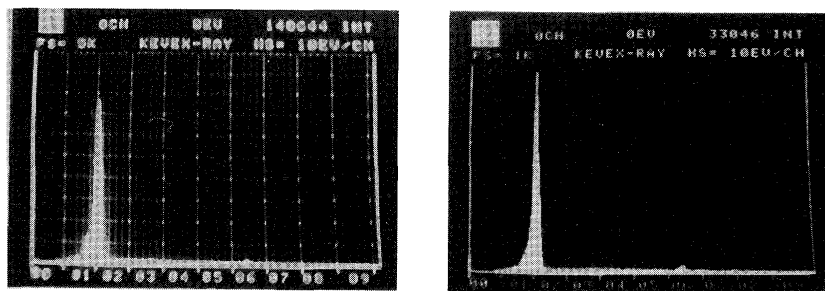


Fig. 2 Scanning electron micrograph and EDX results obtained from zirconia/carbon steel joint.

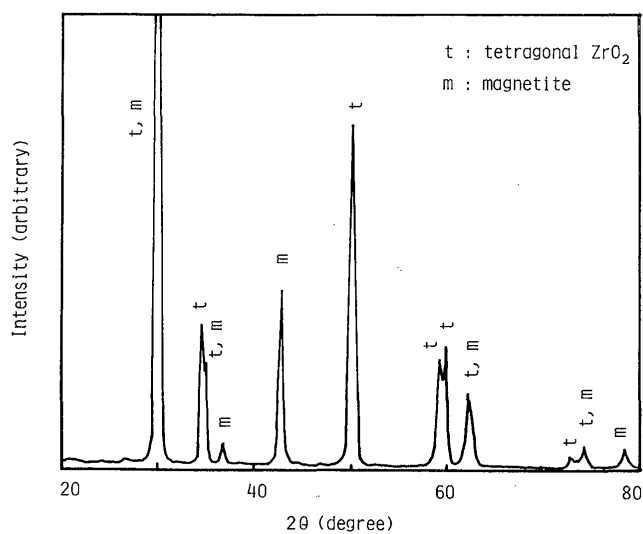


Fig. 3 TFXD pattern obtained from fracture surface of zirconia side of zirconia/carbon steel joint.

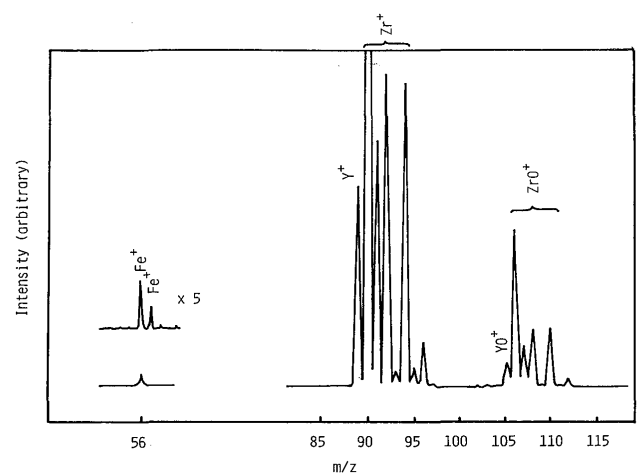


Fig. 4 Secondary ion mass spectrum obtained from the fracture surface of zirconia side of zirconia/carbon steel joint after sputtering for 100 min.

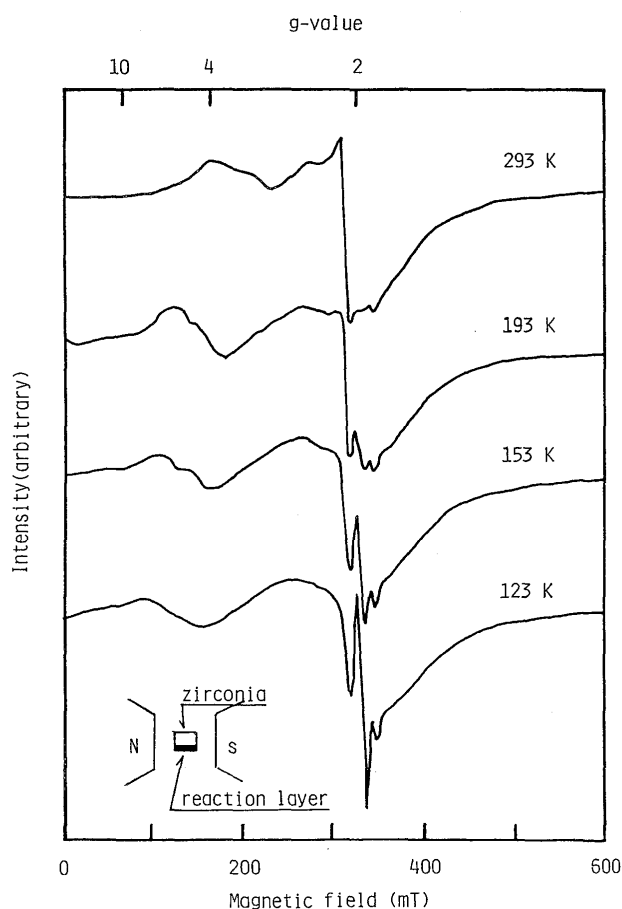


Fig. 5 ESR spectra obtained from zirconia after fractured. (Specimen zirconia was cut into the dimension of 2 mm \times 2 mm \times 8 mm and located so that reacted surface of zirconia was parallel to magnetic field.)

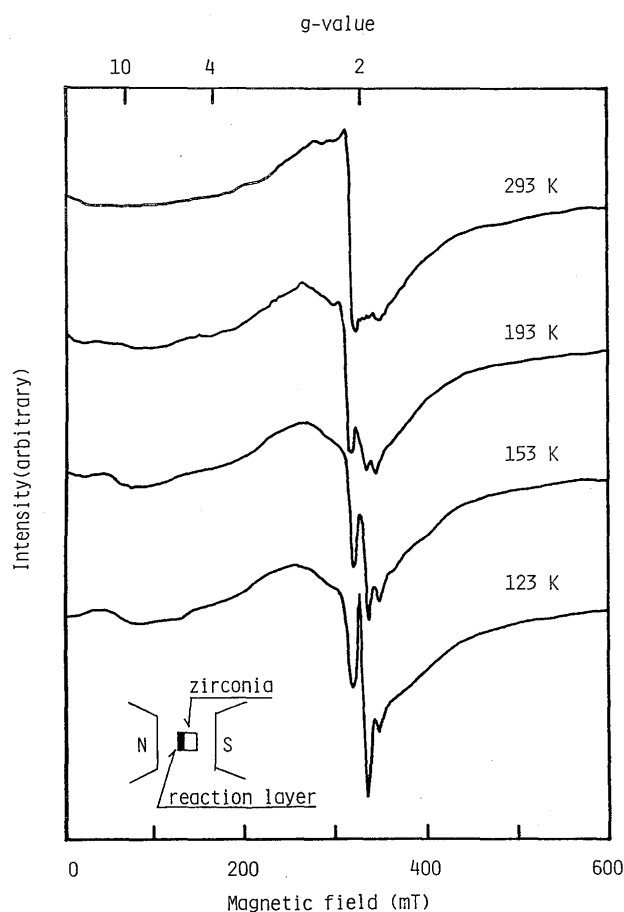


Fig. 6 ESR spectra obtained from zirconia after fractured. (Specimen zirconia was located so that reacted surface of zirconia was perpendicular to magnetic field.)

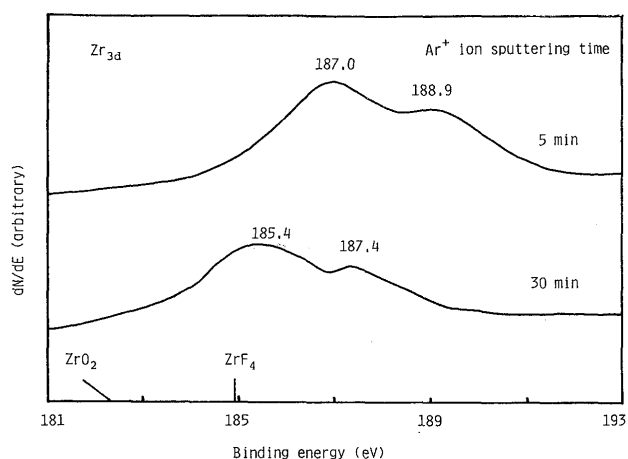


Fig. 7 Photoelectron spectra of Zr_{3d} obtained from the reacted surface of zirconia after fractured.

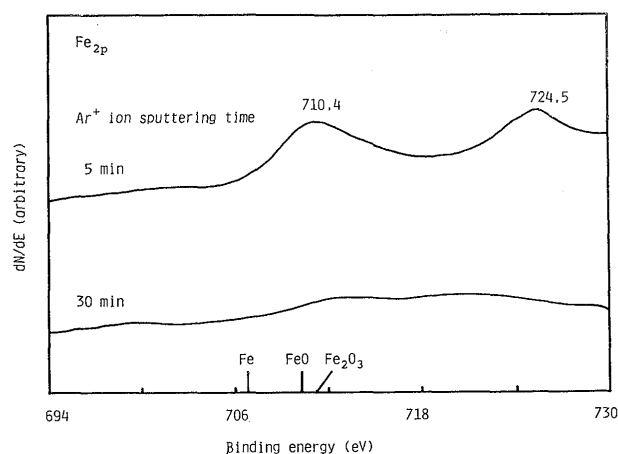


Fig. 8 Photoelectron spectra of Fe_{2p} obtained from the reacted surface of zirconia after fractured.

surface layer of zirconia. Further, taking into consideration the previous results⁹⁾, the broad absorption can be assigned to dipole-interacted Fe^{3+} ions. Above-described three ions are possible candidate ions for sharp absorptions. The formation of Zr^{3+} and Y^{2+} ions can not be neglected on account of reacting zirconia with carbon steel in a vacuum of 10^{-2} to 10^{-3} Pa. The g-value of the

sharp absorption observed at room temperature is about 2.060 though the value is affected by broad absorption. On the other hand, g-value of the sharp absorption appeared with decreasing temperature is about 1.944. It is clear that these sharp absorptions originate from different origins, respectively.

It may be reasonable to assign $g = 2.06$ absorption to

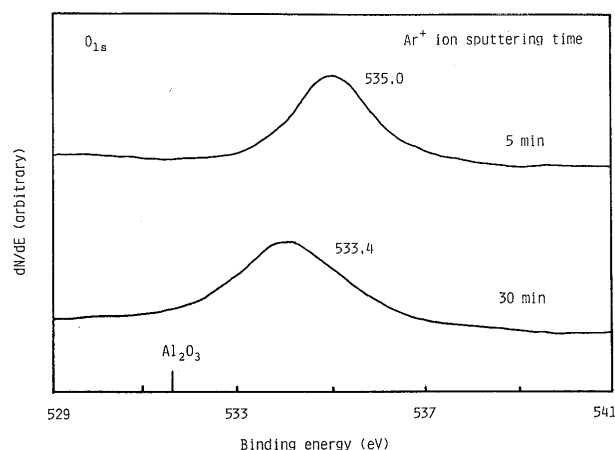


Fig. 9 Photoelectron spectra of O_{1s} obtained from the reacted surface of zirconia after fractured.

isolated Fe^{3+} ions in zirconia lattice, because Fe^{3+} ions in various crystals produce ESR absorption having a g -value larger than 2.000⁶⁾. The small intensity of the absorption suggests low solubility of Fe^{3+} ions into zirconia lattice, which is supported by phase diagram result¹⁰⁾. Weak ESR absorption near 160 mT was clearly observed when reacted surface of specimen was located so as to be parallel to magnetic field. The weak absorption shifted to lower magnetic field with decreasing temperature. Assignment of the absorption remains unclear in the present study, but it may be connected to Fe^{3+} - Fe^{3+} interaction^{11,12)} in magnetite phase on reacted zirconia. Appearance of weak ESR absorption may be related to preferred-orientation of magnetite phase on the interface of zirconia / carbon steel joint. No detection of some peaks in TFXD pattern is probably connected with the dependence of weak ESR absorption on the direction magnetic field. Consequently, large amount of metallic iron near the interface were oxidized by oxygens partly from zirconia and also partly from atmosphere, resulting in forming magnetite phase. Some amount of metallic irons diffused into zirconia lattice in the form of trivalent iron.

It would be reasonable to interpret that $g = 1.944$ sharp absorption originates from Zr^{3+} ions produced by reduction of zirconia by metallic irons. The absorption at $g = 1.906$ was observed in a oxide glass containing zirconium and assigned to Zr^{3+} ions⁸⁾. Trivalent titanium ions in amorphous and crystalline oxides also give a ESR absorption near the g -value of 1.97¹³⁾. Because Zr^{3+} ion is the same outermost electronic configuration to Ti^{3+} ion, it is expected that Zr^{3+} ions give a similar ESR absorption to the case of Ti^{3+} ion, though deviation from 2.0023 (the g -value of free electron) depends on crystal field. From the above consideration, it is concluded to assign the sharp absorption to trivalent zirconium ions which were formed by reaction with metallic iron.

The formation of very thin layer of magnetite is sup-

ported by no detection of Fe_{2p} XPS peaks after sputtering for 30 min. Sputtering rate in the present study was about 1 nm/min and therefore the thickness can be estimated to be about 30 nm. From the chemical shift of $Fe_{2p(3/2)}$ and the value of multiplet splitting of Fe_{2p} levels, chemical state of iron corresponds to a mixed state of trivalent and divalent iron ions¹³⁾. The conclusion shows a good agreement with TFXD result.

Subsequently difference between two O_{1s} binding energies (535 eV and 533.4 eV), equals just to that between two $Zr_{3d(5/2)}$ binding energies (187 eV and 185.4 eV).

Anomalous chemical shifts of O_{1s} and $Zr_{3d(5/2)}$ binding energy may be attributed to partial charging effect on insulating material.

No detailed characterization on reduced zirconia was performed in the present study. New proof on the existence of trivalent zirconium on the interface of zirconia / carbon steel joint is required in further investigations.

5. Summary

Reaction between zirconia (3 mol% Y_2O_3) and carbon steel was studied for purpose of making carbon steel high functional by joining to zirconia. Interface of zirconia / carbon steel was characterized using SEM-EDX, TFXD, SIMS, ESR and XPS methods. TFXD result on surface of zirconia after fractured shows the formation of magnetite phase at the interface of the joint. Observation of broad ESR absorption near $g = 2.0$, which is attributed to Fe^{3+} - Fe^{3+} interaction, shows a good agreement with the detection of magnetite phase. Weak interface between magnetite and metallic iron produces no good strength of the joint. Small ESR absorption $g = 2.06$ was originated from isolated Fe^{3+} ions in zirconia lattice. With decreasing temperature in ESR measurement, a sharp absorption was observed at $g = 1.944$ and the appearance of the absorption is attributed to the formation of trivalent zirconium ions in the interlayer of the joint. Further, the existence of trivalent zirconium ions is a proof of redox reaction between zirconia and metallic iron. TFXD and ESR results show a good agreement with the chemical state of iron determined by XPS method. No observation of Fe_{2p} XPS peaks after sputtering for 30 min shows that the thickness of magnetite phase is below 30 nm.

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