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Alumina–copper joining by the sintered metal powder process

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Abstract

Sintered metal powder process (SMPP) is one of the high technology methods in ceramic–metal joining domain. The present study examines the effect of temperature and time of metalized layer sintering on the thickness and homogeneity of the joining layer, the leakage rate in alumina–copper joining zone, and also identifies the different phases formed during sintering. The samples were characterized by optical microscopy (OM), scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS). Microstructure studies indicate that sintering the metalized layer with a holding time of 90 min at the temperature of 1530 °C, and with an applied layer thickness of 50 μm with proper plating and brazing stages lead to a completely homogeneous joining zone with an adequate thickness (about 33 μm). The results of leak tests on alumina–copper specimen in this condition was less than 10^{-9} Pa l s^{-1}.

Keywords: A. Joining; B. Electron microscopy; Sintered metal powder process (SMPP); Alumina

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1. Introduction

During the last thousand years, man has tried different methods for producing strong and secure ceramic–metal joints [1], but developments in industrial processes were achieved in the 1980s [2].

From a theoretical point of view, a wide range of methods are applicable for ceramic–metal joining; but because of differences in the physical and chemical structures of ceramics and metals only a few methods can be used. One of the methods which results in sound joints between ceramic and metal is coating a Mo–Mn layer on alumina surface and sintering the metalized layer before brazing. This method is known as sintered metal powder process (SMPP) [3]. In first attempts, Pulfrich [4] introduced a mechanism for ceramic–metal joining in 1930. In later years scholars such as Pincus, Cole, Hynes and Denton [5], introduced some studies on phase formation during sintering and the effect of glassy phases on metalized layer adhesion. Floyd investigated the effect of particle size on the metalized layer adhesion [5].

The metalized layer formula in the Mo–Mn process consists of a mixture of Mo and Mn powders with some glassy compounds and a solvent which is applied in the form of slurry on the ceramic surface [6–9]. The main purpose of SMPP is wetting the ceramic surface for brazing. After sintering the metalized layer, in order to increase the surface wetness and avoid any attacks between the created joint of alumina and Mo–Mn layer by filler braze, metalized layer must be plated [10]. Main advantages of SMPP are applicability for large number of samples, lower cost, less sensitivity to process parameters against other brazing techniques like active metal brazing, good results in leak tests, and wide usage for alumina as most applicable ceramic. Numerous process steps is the main disadvantage of this process.

Successful ceramic–metal joining depends on different factors such as: joining zone thickness, phase formation during sintering, metalized layer morphology, conditions of plating and brazing. Thus, to have a secure joint between ceramic and metal, accurate investigation of effective factors should be taken into consideration [11].

In the present research, the effects of temperature and time of metalized layer sintering on the thickness and homogeneity of joining layer and alumina–copper joining zone leakage rate have been studied based on metalized layer applied composition.

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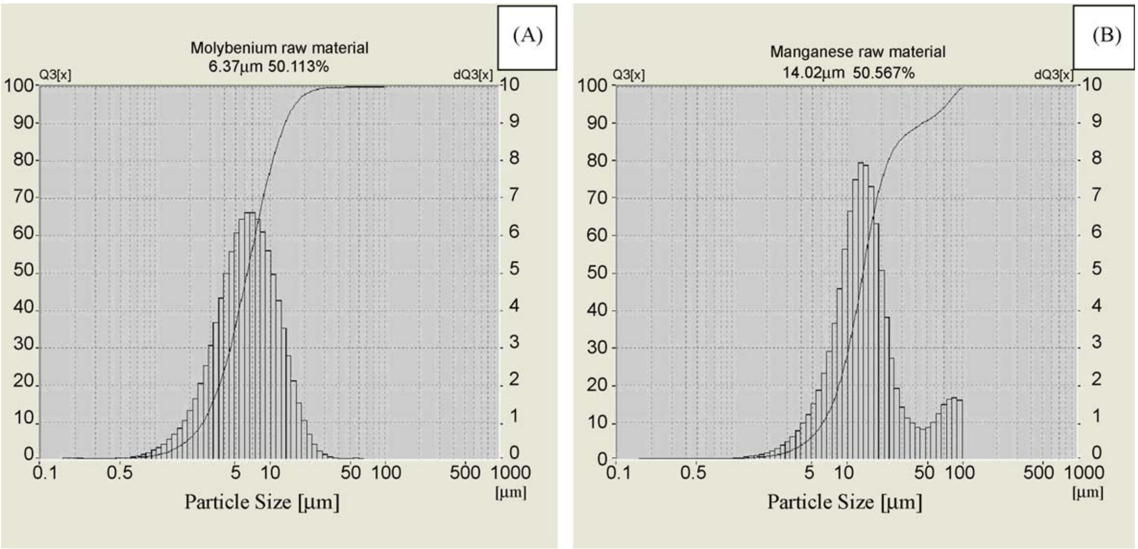

Fig. 1. Laser particle size distribution of (A) Mo and (B) Mn powder.

2. Experimental procedure

The slurry was made of Mo, Mn, Al_2O_3, CaO and SiO_2 99.99% pure powders. Particle size distributions of Mo and Mn powders are shown in Fig. 1. Butyl acetate, nitro cellulose and butyl oxalate used in the slurry were provided as high purity materials as well. Sintering was carried on in a 1500 °C furnace with 6 l capacity under hydrogen atmosphere.

Ceramic discs samples with $d = 25$ mm and $H = 7$ mm dimensions were cleaned in an ultrasonic set which contains F.E.P. solution, then washed in 50% pure HCl solution for 5 min. To make the required slurry, a combination of 70% Mo powder, 10% Mn powder, 5% SiO_2 powder, 3% CaO powder and 12% Al_2O_3 were mixed. Butyl acetate, nitro cellulose and butyl oxalate were added to the mixture. The prepared slurry mixture was ball milled for 48 h. The slurry was painted on the surface of alumina by a painting brush. The applied layer on the surface of sample is between 25 and 50 µm thick. The sintering of metalized specimens was conducted in a furnace under wet hydrogen atmosphere. Sintering temperatures were 1400, 1470, 1530 and 1600 °C with holding times of 40, 60 and 90 min. After primary sintering process, the metalized layer surfaces were nickel plated about 5 µm thick by electroplating method. Electroplating process was carried out using 300 g/l $NiCl_2$, 30 g/l H_3BO_3 solution with pH about 4–5 at room temperature. In order to achieve plating layer with thickness of about 5–7 µm, current density of 5.5 A/m^2 were used for 40–50 min. Samples were then sintered under wet hydrogen atmosphere, again. At the end, Ag (75%)–Cu (20%)–Pd (5%) filler with $d = 15$ mm and $H = 0.5$ mm dimensions was inserted between alumina and high free oxygen copper (HFOC) in $d = 25$ mm and $H = 5$ mm dimensions. The samples were conducted in a furnace under the hydrogen atmosphere for brazing process.

Leak test was done on all samples in order to calculate the leakage rate between alumina and copper joining zone based on ASTM F19-64 [12]. The brazed test specimen were vacuum-leak checked on a conventional helium spectrometer-type leak checker with sensitivity of 10^{-9} Pa l s^{-1} at standard temperature and pressure. The samples were subjected to an atmosphere of helium for 0.5–5 min. The analysis of the structure of inter-layers of alumina and copper and the investigations on the effects of temperature and time of sintering on the final thickness and homogeneity of the joining zone were conducted by scanning electron microscopy and energy dispersion spectroscopy (Philips, XL30 Series). To study phases' formation during metalized layer sintering, XRD test was taken on 9 same slurry solutions that were sintered in different conditions with different temperatures of 1000, 1470 and 1530?C and time durations of 40, 60 and 90 min using X-ray diffraction analysis (Philips, MPD-XPERT, λ: Cukα = 0.154 nm).

Fig. 2 indicates a diagram of the experimental procedure.

3. Results and discussion

3.1. Thickness and homogeneity

The effect of time and temperature of sintering and the thickness of applied layer on the leakage rate and the thickness of joining layer are listed in Table 1. As shown in Table 1, the layer thickness increases by increasing the holding time at each temperature with slow thickness growth rate.

When the thickness of the applied layer is 50 µm, the final thickness of the joining layer is larger than the thickness obtained with the use of the 25 µm applied layer. This is because interdiffusion can occur through 50 µm layer. Both Helgesson [4] and Takahashi and Okabe [10] mentioned that the applied layer thickness should be between 40 and 70 µm. Thin layers lead to weak joints and small width of the interface zone, and if the thickness is higher than the allowed limit, a high amount of applied layer would not get involved in the interaction with alumina, thus, a proper bonding would not occur between Mo–Mn and alumina.

Table 1 and Figs. 3–5 show the effect of temperature on the thickness of joining zone. As seen, the effect of

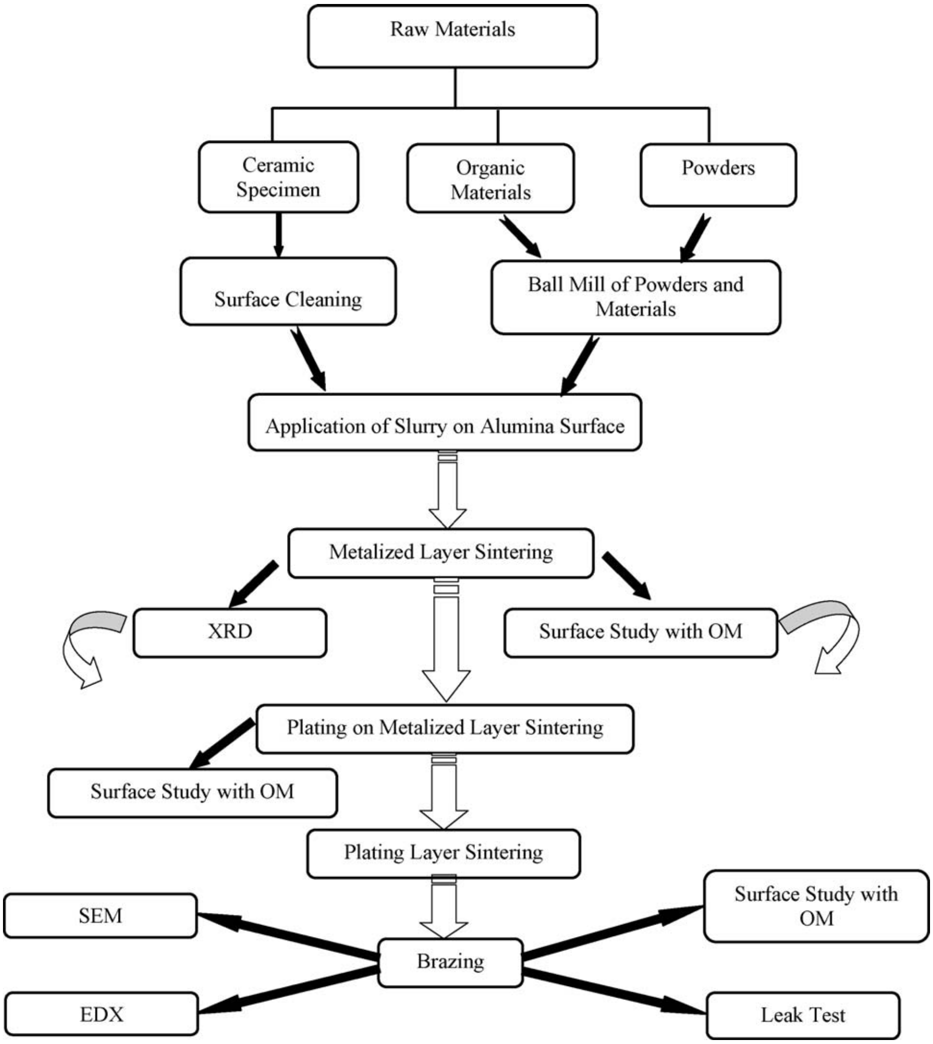

Fig. 2. Schematic chart of experimental procedures.

Table 1
Effect of (a) time; (b) temperature of metalized layer sintering; (c) thickness of applied layer on the leakage rate and thickness of joining layer.

Temperature (°C)	Time (min)	Applied layer thickness (μm)	Joining layer thickness (μm)	Leakage rate (Pa l s^{-1})
1400	40	25	4.76	10^{-3}
	60		4.97	10^{-4}
	90		6.49	10^{-5}
1470	40		10.38	10^{-5}
	60		11.25	10^{-6}
	90		12.12	10^{-6}
1530	40		14.46	10^{-6}
	60		15.27	10^{-7}
	90		16.73	10^{-7}
1400	40	50	9.30	10^{-5}
	60		9.95	10^{-5}
	90		13.38	10^{-6}
1470	40		18.34	10^{-8}
	60		20.11	10^{-8}
	90		20.33	10^{-8}
1530	40		21.84	10^{-9}
	60		24.54	10^{-9}
	90		32.70	10^{-9}

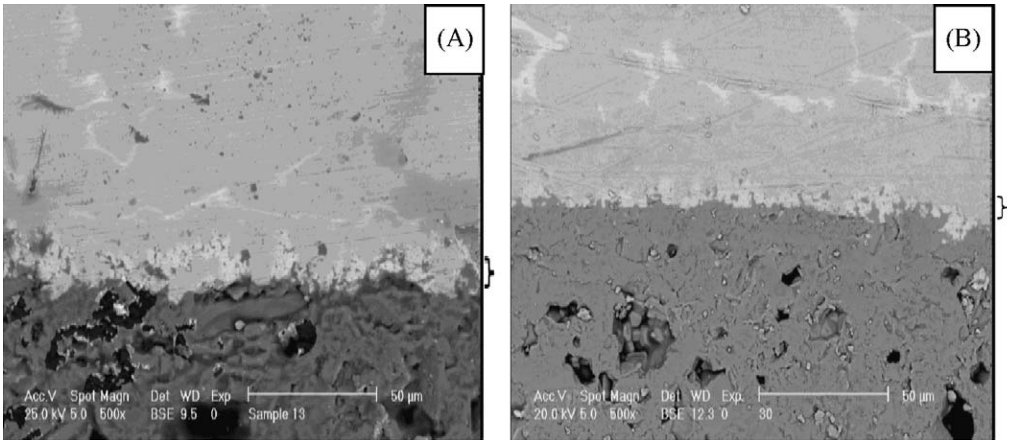

Fig. 3. Scanning electron microscope figure of a specimen with the sintering temperature of 1400 °C, applied layer thickness of 50 μm and sintering time of (A) 60 min and (B) 90 min.

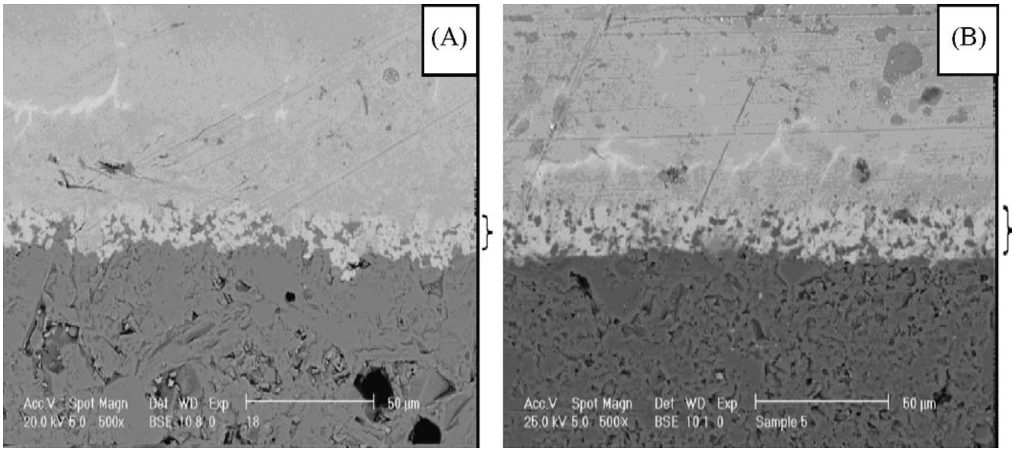

Fig. 4. Scanning electron microscope figure of a specimen with the sintering temperature of 1470 °C, applied layer thickness of 50 μm and sintering time of (A) 60 min and (B) 90 min.

temperature is more significant than time. The joining process depends on interdiffusion in which diffusion itself depends on temperature and time, and the role of temperature in this case is more important than time. Therefore, increasing temperature is an effective factor for increasing the joining layer thickness. However it should be mentioned that the specimens with sintering temperature of 1600 °C were blistered because of high sintering temperature of

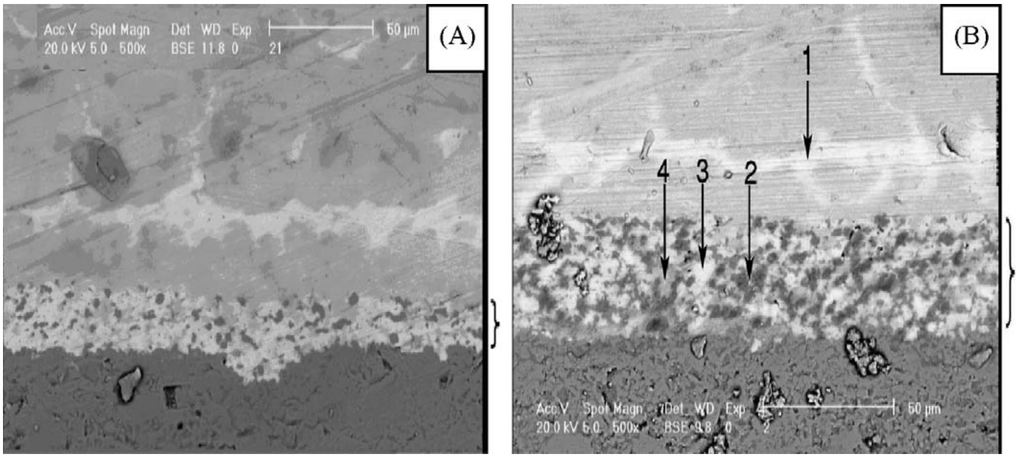

Fig. 5. Scanning electron microscope figure of a specimen with the sintering temperature of 1530 °C, applied layer thickness of 50 μm and sintering time of (A) 60 min and (B) 90 min.

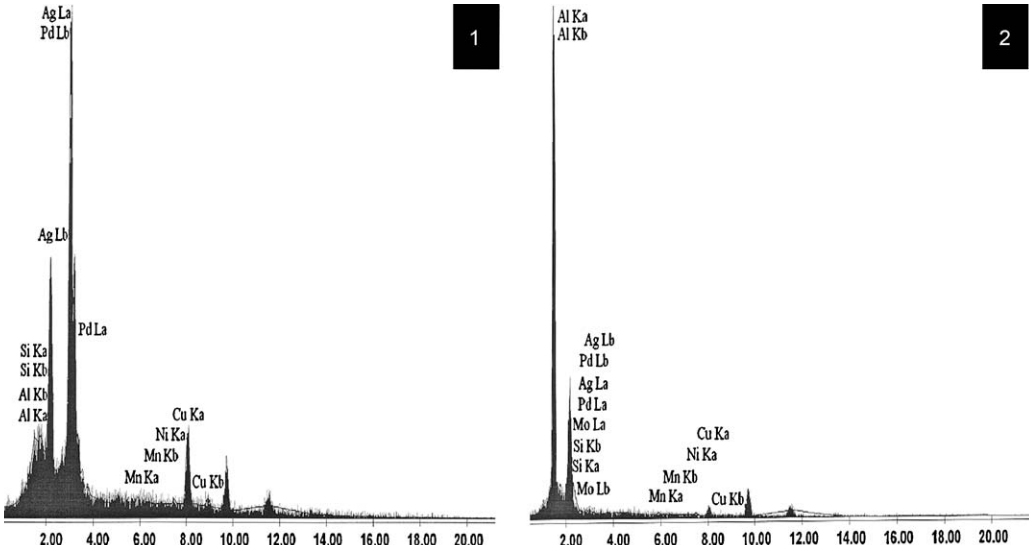

Fig. 6. Elemental microanalysis of points 1 and 2 shown in Fig. 5B.

metalized layer; therefore it was impossible to continue the rest of the processes on them.

As shown in Figs. 3–5, by increasing the holding time and temperature, an interfacial layer with maximum homogeneity and distribution of phases is obtained. In this case the effect of time is larger than temperature. In fact, temperature is the driving force in this joining and time contributes to homogeneity and stability.

The results reveal that the best condition of thickness and homogeneity in the joining zone occurs with a sintering temperature of 1530 °C, 90 min holding time and with a 50 μm thick applied layer.

Figs. 6 and 7 both show the elemental microanalysis of different points of alumina and copper interlayer zone. Generally, the figures reveal that the white zones are related to Mo, the black zones to alumina, the grey zones to glassy phases and the white vein to silver.

The nickel plated layer before brazing is shown in Fig. 8. Destruction of this layer after brazing can be seen in Figs. 3–5. Studies reveal that since all fillers have low corrosion resistance and high activity, the Ag (75%)–Cu (20%)–Pd (5%) filler has damaged the Nickel plated layers. In some zones, the filler can damage the joint between alumina and Mn–Mo layer as well with high corrosion rate of the filler material [4]. This can be attributed to the small size of Ag atoms and to their high diffusion coefficient. They diffuse in copper and create white veins areas. In all figures, these veins are visible 20 μm away of the Mn–Mo layer and the analysis of these zones is very similar to the analysis of the applied filler (Fig. 6(1)).

3.2. Leak test

The leakage rate of each specimen is reported in the last column of Table 1. An acceptable leakage rate range is less than

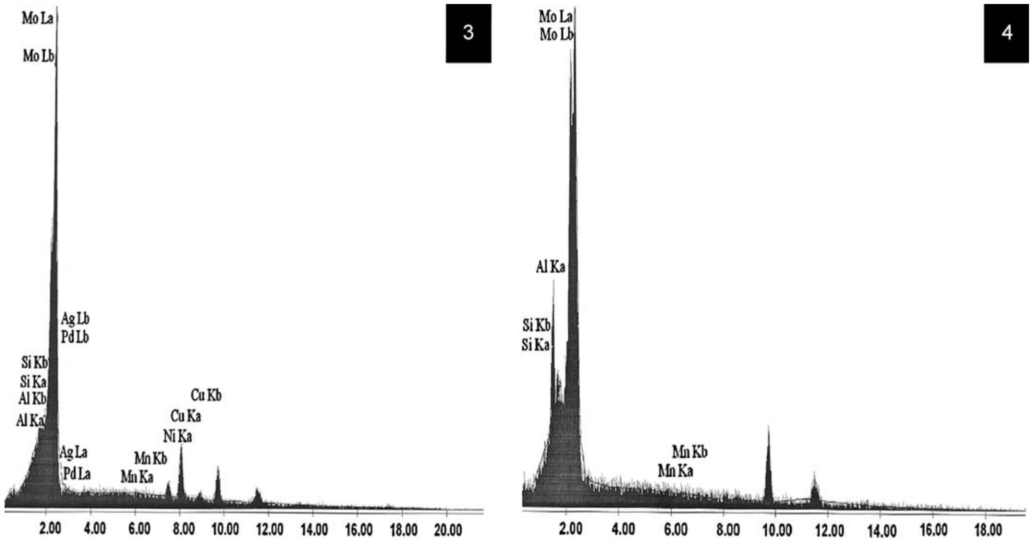

Fig. 7. Elemental microanalysis of points 3 and 4 shown in Fig. 5B.

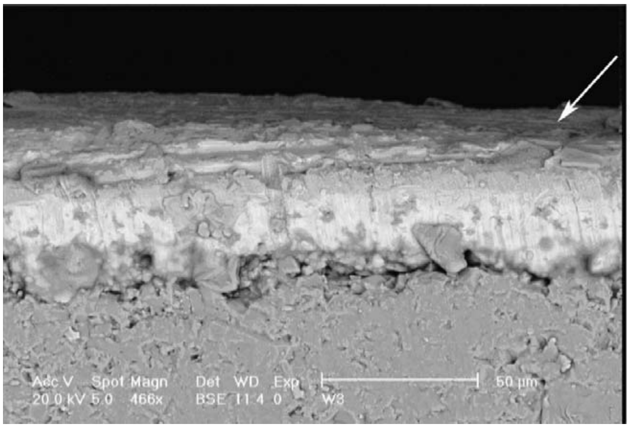

Fig. 8. Scanning electron micrograph of a specimen with the sintering temperature of 1530 °C, sintering time of 90 min and applied layer thickness of 50 µm.

10^{-9} Pa l s^{-1} [12]. As shown in Table 1, specimens with an applied layer of 25 µm thick are not acceptable. All specimens which were sintered in 1530 °C with the applied layer thickness of 50 µm passed this test successfully. The proper sintering temperature has created proper joining between the metalized layer and alumina. The result reveals that the thickness of applied layer and then sintering layer temperature are the most significant factors controlling the leakage in specimens. The holding time has no significant effect.

3.3. X-ray diffraction

The X-ray diffraction patterns show formation of Galaxite ($MnO{\cdot}Al_2O_3$) with presence of Molybdenum and alumina from the primary slurry in the sintered layer (Fig. 9). The sintering temperature is a significant factor in the mechanism of joining layer formation between alumina and metalized layer. The joining between the metalized layer and high purity alumina has two different mechanisms: (a) ion exchange between Mo^{6+} and Al^{3+} with diffusion of Mo into alumina and (b) formation of Galaxite ($MnO{\cdot}Al_2O_3$) phases. The formation of Hausmonite (Mn_3O_4) occurs by the oxidation of Mn atoms in the metalized layer. Diffusion of Mn_3O_4 along alumina grain boundaries proceeds by increasing temperature. At about 1400 °C, the Galaxite, with melting point temperature of 1520 °C, is directly sintered from alumina and Hausmonite. Since the Mo particle sizes are smaller than alumina particles, the melted Galaxite return back and get locked in metalized layer. This phenomenon occurs based on capillary force principle. The presence of solid Galaxite on the surface of alumina particles, increase the surface adhesion and from strong mechanical joining with Mo [4]. It seems that choosing a temperature of 1530 °C supplies the best condition for joining, because at this temperature, Galaxite phase melts and can return to metalized layer through Mo particles interspaces and make a proper bond with Mo phase.

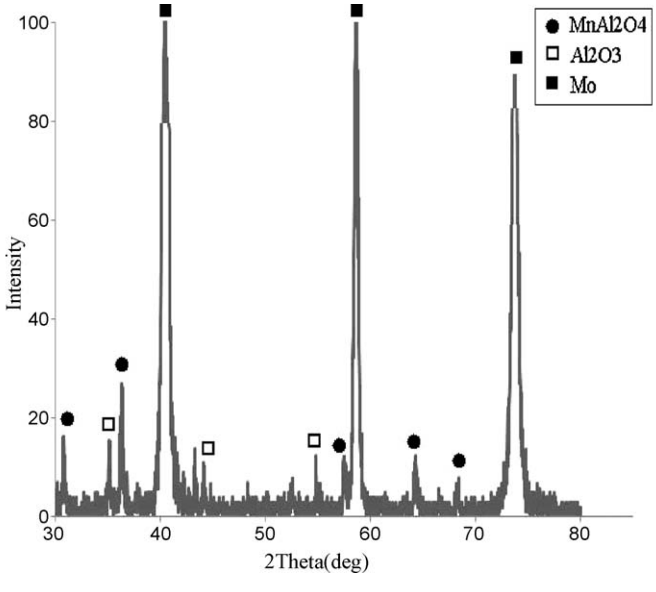

Fig. 9. X-ray diffraction pattern of metalized layer during sintering at a temperature of 1530 °C and time of 90 min.

4. Conclusions

(1) The best applied layer thickness for joining alumina to copper based on proper binding and less leakage rate is 50 µm thick.
(2) The effect of temperature on diffusion and increasing the joining layer thickness is more significant than of time while the effect of time to gain a proper homogeneity in the joining zone is much more important than the effect of temperature.
(3) The best sintering time and temperature to arrive at a proper thickness and homogeneity in 99% pure alumina/copper joints are 1530 °C with 90 min holding time in which the thickness of joining zone is over 32.70 µm.
(4) In order to avoid leakage in specimens, the most significant factor is the applied layer thickness and then the sintering temperature.
(5) The sintering time does not play a significant role in the success of leak test.
(6) The best conditions for the least leakage rate are: a temperature of 1530 °C, a sintering time of 90 min and an applied layer thickness of 50 µm for sintering.
(7) The formation of a Galaxite phase occurs at temperatures higher than 1400 °C.

References

[1] M.G. Nicholas, Ceramic–Ceramic and Ceramic–Metal Joining, Chapman & Hall, UK, 1989.
[2] K. Suganuma, Strength and microstructure of silicon nitride aluminum interface fabrication by squeeze cast brazing, Journal of European Ceramic Society (11) (1993) 43–49.
[3] M.G. Nicholas, T.H. North, Material aspects of ceramic–ceramic and ceramic–metal bonding, in: Advanced Join Technology, Chapman & Hall, UK, 1991.
[4] C.I. Helgesson, Ceramic to Metal Bonding, Boston Technical Publisher, USA, 1968.
[5] S.J. Schneider, Engineered Materials Hand Book, Ceramics and Glasses, vol. 4, ASM International, Metals Park, OH, 1998, pp. 504–506.
[6] M.G. Nicholas, Joining of Ceramic, Chapman & Hall, UK, 1990.

[7] L. Belic, K. Alenkas, Synthesis reactions and thermodynamics of compound formation during Mo–Mn layer sintering, in: Electronics and Vacuum Technique, 1995 Slovenia, pp. 125–129.

[8] M. Schwartz, Brazing for the Engineering Technologist, Chapman & Hall, UK, 1984.

[9] D. Chatain, V. Getta, Wetting and interfaces in metal-oxide system, in: Interfacial Science in Ceramic Joining, NATO Scientific Affairs Division, 1994, London, pp. 45–57.

[10] M. Takahashi, M. Okabe, Study on optimum thickness of interlayer in ceramic–metal joining, in: Ceramic to Metal Joining, Cambridge Scientific Abstract Publishers, Cambridge, 2000 , pp. 905–911.

[11] I. Foroutan, Joint Ceramic–Metal Based on Sintered Metal Powder Process, Shiraz Navid Publisher, Iran, 2007 (In Persian).

[12] R.L. Meltzer, R.A. Storer (Eds.), Annual Book of ASTM Standards, 10.04, Easton, Philadelphia, 1988, pp. 97–100.