

THE STUDY OF THE THERMAL PROPERTIES OF SPINEL NICKEL ALUMINATE

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ABSTRACT :-

Spinel nickel aluminate is an important industrial material, has been synthesized by a solid state reaction method from nano powders γ - Al_2O_3 and NiO represented as a theoretical batch. Sintering the raw materials was done at rate heating 4 °C/min in 1500 °C. The sintered specimens were investigated employing by X-ray diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDS) and scanning electron microscopy techniques (SEM). It is that the formation nickel aluminate spinel was completed in 1500 °C, at the following percent (20 wt % NiO and 30wt% NiO and 50 wt% NiO), thermal properties have been also investigated for sintered specimens. The new composite materials it high thermal expansion stability and resistant to thermal shock at 1200°C, especially with 30 wt % NiO.

Keywords: XRD; SEM; EDS; Al_2O_3 -NiO nano particle; spinel nickel aluminate ($NiAl_2O_4$).

دراسة الخواص الحرارية للسبيل نيكال الومينيت
الاء حسن فاضل محسن اسود احمد عودة

الخلاصه :

سبيل نيكال الومينيت هو ماده صناعيه مهمه ، حضرت بطريقه تفاعل الحاله الصلبه من مكوناتها الاساسيه وهي كا ما الومينا واوكسيد النيكال . تم تلييد المواد الأوليه عند دورتين حراريتين وعند معدل حراري يبلغ (4 °C/min) تم تشخيص العينات الملبدة باستخدام تقنيات الأشعة السينية (X-ray) وكذلك المجهر الالكتروني الماسح (SEM) ، وان التفاعل اكتمل عند 1500 °C . تم دراسة الخصائص الحرارية لهذه المادة المركبة حيث انها تمتاز بالاستقرار الحراري من خلال فحص التمدد الحراري عند كل نسب الخلط ، اضافه الى مقاومه العاليه للصدمة الحراريه عند 1200 بالاخص عند اضافه 30 wt . % NiO

1. INTRODUCTION.

There is a correlation between the structures and properties of materials. To identify the characteristic of the material and its appropriate applications, where for need to apply it is at the specific circumstances through knowledge of the properties and behavior of a range of materials, manufacturing a composite material of alumina and nickel oxide, known nickel aluminate (NiAl_2O_4) has excellent strength and good wet ability with metals at high temperatures [Erno E. & Goran C, 2013] , in addition to the general merits of spinel materials, for its thermal stability, as well as the catalytic activity . Nickel aluminates (NiAl_2O_4) is one of the most important aluminate materials that have been used for many applications, including magnetic materials, pigments, catalysts and refractory materials [Mocal K. & Navrotsky J, 1989, Sang- Jin Lee & Sang-Ho Lee , 2013] .In particular, nickel aluminate having a skeleton structure can be applied to a new fabrication method for metal - ceramic composites. The nano powders $\text{NiO-Al}_2\text{O}_3$ oxides system finds broad application in a number of important industrial catalytic processes as steam reforming, partial oxidation of methane meth- nation of carbon monoxide and hydrogenation of unsaturated organics [Deraz N. M. 2013, Wang H, Tian X, 2004].

These catalysts have perspective in future technologies as dry reforming of methane with carbon dioxide and tri-reforming. Alumina supported nickel oxide as a nano composite material is also interesting for ceramic industry, as well as humidity sensors and mine-safety sensors [Makhlouf S.A . & KhalilM.S., 2003]. The mechanical powder mixed samples were prepared by mixing of the commercial at particle size (20 nm) $\gamma\text{-Al}_2\text{O}_3$ with a commercial NiO at particle size (20 nm). The metal oxide powders were homogenized planetary ball mill mixer at a different NiO percentage [Ragupathi C ., Judith J. V.L., 2014] . Therefore, in this study have been added the nickel oxide to alumina for the manufacture composite material is called spinel nickel aluminates (NiAl_2O_4) resulting from their interaction ,for the purpose of obtaining excellent physical and thermal properties. The aim of this study to prepare nickel aluminate via solid state reaction by sintering at high temperature. Another goal is to study of the thermal properties of spinel form on the structural and morphological properties of the as prepared nickel aluminate. The techniques employed were XRD, EDS and SEM.

2. EXPERIMENTAL PROCEDURE :

2.1 Materials.

Two $\text{Al}_2\text{O}_3/\text{NiO}$ mixed oxides were prepared by mixing calculated proportions of nickel and aluminum oxides with polyvinyl alcohol. In experimental, the ratios of the nickel oxides were 20 wt%, 30 wt% and 50 wt% , was formed the samples when compressed in stainless steel mold using hydraulic press (cold die pressing) by uniaxial pressure device. The samples were pressed in a rectangular mold with dimensions (6 cm×6 mm×5 mm) , after that the samples was dried at temperature 105°C for 24 hours in a oven drying using electric blast dry box (WG43) to remove inorganic binder material and moisture. The samples was placed in a container high purity alumina sagger (Shangtao brand) for sintering process as well as avoid cracks and gaps, subsequently were sintered the samples at 1500 °C at heating rate 4°C/min. Fig. (1) shows the equilibrium phase diagram of spinel nickel aluminate (NiAl_2O_4) which have been relying on the mixing ratios between alumina and nickel oxide.

2.2. Techniques.

An X-ray measurement of various mixed solids was carried out using a shimadzu 6000, Japan) at (College Engineering Material / University of Babylon). The patterns were run with Cu K α radiation at 40 kV and 30 mA with scanning speed in 2θ of 6° min^{-1} . The crystalline distance of NiAl₂O₄ present in the investigated solids was based on X-ray diffraction line broadening and calculated using Bragg's law as shown in Equation (1) . [Bragg's law2002].

$$n\lambda = 2d \sin \theta \quad (1)$$

Where, n is an integer, λ is the wavelength of incident wave, d is the spacing between the planes in the atomic lattice, and θ is the angle between the incident ray and the scattering planes.

The all samples sintered were examination of the microstructure scanning electron microscopy (SEM) in Islamic Republic of Iran were recorded on TESCAN Company –country Czech. The samples were dispersed in ethanol and then treated ultrasonically in order disperse individual particles over a gold grids. They scan surface sample with high energy beam of electron .Photographs with a magnification up (500KX). But Energy Dispersive X-ray spectrometry (EDS) is RONTEC Company from USA.

3. RESULTS AND DISCUSSION :

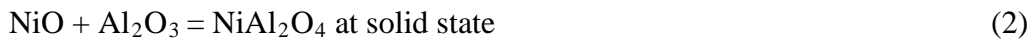
3.1 Mineral analysis.

X-ray diffraction technique was used identify, the phases were used done by X-ray diffraction analysis with a scan range (10° - 80°) and a step size of 0.02° , scanning speed in 6 deg /min .To identify the basic components of the samples sintered, and making sure that the occurrence interaction between alumina and nickel oxide in all mixing ratios used, at a pressure of 175 MPa with added of 2% P.V.A as a binder, were sintered 1500°C for 14hrs with an average heating rate of $4^\circ\text{C} /\text{min}$. The X-ray diffraction patterns of samples containing different amount of NiO. For experimental work, there are principal peak of high sintering temperature (Al₂O₃) and (NiAl₂O₄), in Fig. (2) shows only peaks of Al₂O₃ and NiAl₂O₄, which shows NiO reacted with Al₂O₃ to form NiAl₂O₄ through a solid reaction at 1500°C , all result of Tables , according to the using Bragg's law [Bragg's law 2002] .Table (1),(2) and (3) explain the XRD data at all nickel oxide percentages for form phases.

The NiO-Al₂O₃ binary phase equilibrium diagram presented and stated that at 1500°C , at the (20 wt% and 30wt%) of nickel oxide, NiAl₂O₄ and Al₂O₃,they are the only phases present at equilibrium state, but in 50 wt %NiO only content nickel aluminate spinel. By stoichiometry, the compositions of the final products were explained by the XRD patterns .Spinel nickel aluminate was prepared by solid state reaction method, it was the explained crystal plane of (220), (311),(400), (422) ,(511) and (440) by miller index.

3.2. The morphology study.

The spinel phase distribution is homogeneous and the outer part of the sample, only the spinel phase located with alumina was observed. Fig. (3) shows the SEM examination. However the dependence of the microstructures, especially interfaces, on the properties of composites is not well understood yet. Moreover, raw materials interfaces used in the formation of this spinel, the play a crucial role in tailoring the composite properties [Konopka K., Litynska L and Dutkiewicz J., 2013]. Shows Fig. (3 a,) that there are homogenous large between the grain with high densification and very little amount of pores and it cleared in Fig. (4) which appeared the energy dispersive of X-ray (EDS). Which that the indicates good for interaction between powders to form spinel nickel aluminate at this ratio addition, to non-appear of pores, in figure (5) and (6) for images (b,c) in SEM. Despite, the image (b) when analyzing (EDS) has the appearance of small amounts of alumina is nonreactive with nickel oxide. In images (c,) show it to be form spinel phase is not bulk material as distributed less homogeneity, the existence of quantities of non-reactive as a Figs. (5) and (6) respectively. Alumina grains are also showing lower granular size; because of alumina grains at higher sintering will grain growth. It is clear from this that the reaction was completed at this sintering temperature evidenced by the appearance spinel phase at each ratios solid state. In order to calculate the amount of the spinel from the raw materials the following reaction of spinel formation was assumed [Kaimin Shih, James O., 2007, Nazemi M.K, Sheibani R. S., V, A ., 2012].



3.3 Thermal properties.

This examination included of thermal expansion coefficient and thermal shock.

3.3.1 Thermal expansion.

Thermal expansion values vary depending on the material being heated. The ratio of coefficient thermal expansion indicates how much a material expands per 1°C , rise in temperature. The figs. (7), (8) and (9) shows typical thermal expansion curve of samples sintered at 1500°C , the samples (20, 30 and 50) wt% NiO. Since cubic nickel aluminate is a very stable material, the effect of cubic NiAl_2O_4 on the thermal expansion coefficient of the prepared raw materials ceramic is show CTE increase with NiO content, but this increase can be considered as noticeable fact that the binary system more complex than simple systems. In general, that the thermal expansion of nickel aluminate increases with increasing temperature, as is evident in the three chart starting from the degree to which the change starts 100°C up to 800°C in the air. that the difference between each grade 25°C , in the figure (8) show that there is a very slight decrease of the 350°C and 400°C , respectively, and then return the item to stability, in a straight line, this due to the result of shrinkage of the resulting after the firing with a high temperature, thus result a slight difference dimensions samples at different rates and that the additive causes little expansion distortion values as well as the pores resulting from spinel phase be developed, at (20 wt %, 30 wt % and 50 wt % NiO) shows that it has developed a new, the strong connectivity between atoms and high thermal stability therefore, thermal expansion depends on each of the following:

1. The expansion is not depend only by the kind of bond, but also by the crystal structure, complex structures have lower thermal expansion than simple structures.

2. Particular, depend on structure material, have to consider the presence of defects, impurities, and porosity as these all affect generally of thermal properties.

the coefficient thermal expansion was calculator, according to equation (3), assuming negligible effect of pressure can be written according to ASTM standard: E228-11.

$$\alpha = [1/L_0 (\Delta L / \Delta T)] \quad (3)$$

Where, L_0 represent, the original length with the temperature change from T_0 to T_f . The parameter α coefficient thermal liner expansion (CTE) and units of reciprocal temperature ($^{\circ}\text{C}^{-1}$) was such as [mm/mm .C] or $10^{-6}/^{\circ}\text{C}$.

3.3.2 Thermal shock.

The thermal shock test was conducted to spinel nickel aluminate. By heating samples prepared in an electric furnace and to different degrees ranging about (500 °C, 1000 °C and 1200 °C) , the time heating for each ranges from temperature one hours (This means that the time constant and of the different heating degree), after quenching samples placed in cold water for the purpose of knowing resistant samples to thermal shock, It has been knowledge samples resistance of thermal shock by compare physical properties and hardness before and after thermal shock at all test ratio . The physical properties represented for porosity and water absorption. The mechanical properties represented for hardness. Table (4) showed the physical properties and hardness before thermal shock.

This is seen from that nickel aluminate resistance to shock at 500°C, through the emergence of a slight difference in hardness and physical properties before and after exposure to this degree sample. Either at 1000°C and 1200°C spinel phase has remained on its resistance despite a slight decrease in its physical properties.

Finally, the spinel remains resistant to thermal shock without cracking as shown in figure (10) at 30wt% NiO for 1200 °C and is attributed to the segregation between them result of non-agglutination granules with each after exposure to the sudden change temperature, thus generate pores which are affected by the high factor thermal properties.

Tables (5), and (6) shows physical and micro hardness properties respectively of the samples after shock, where it the better proportion to thermal shock in 1200°C at 30 wt%NiO, figs. (11), (12), (13), (14), (15) and (16) shows the apparent thermal shock in 500 °C,1000 °C and 1200 °C respectively .

4. CONCLUSIONS :

Spinel nickel aluminate has been synthesized by a solid state reaction method from γ - Al_2O_3 and NiO .The powder XRD data obtained on NiAl_2O_4 powder are in good agreement with the standard reported data by Bragg low.

The SEM images show the presence of fluffy morphology found in the powder. The obtained samples have a homogenously distributed species high thermal expansion stability and resistant to thermal shock at 1200°C, especially with 30wt% NiO.

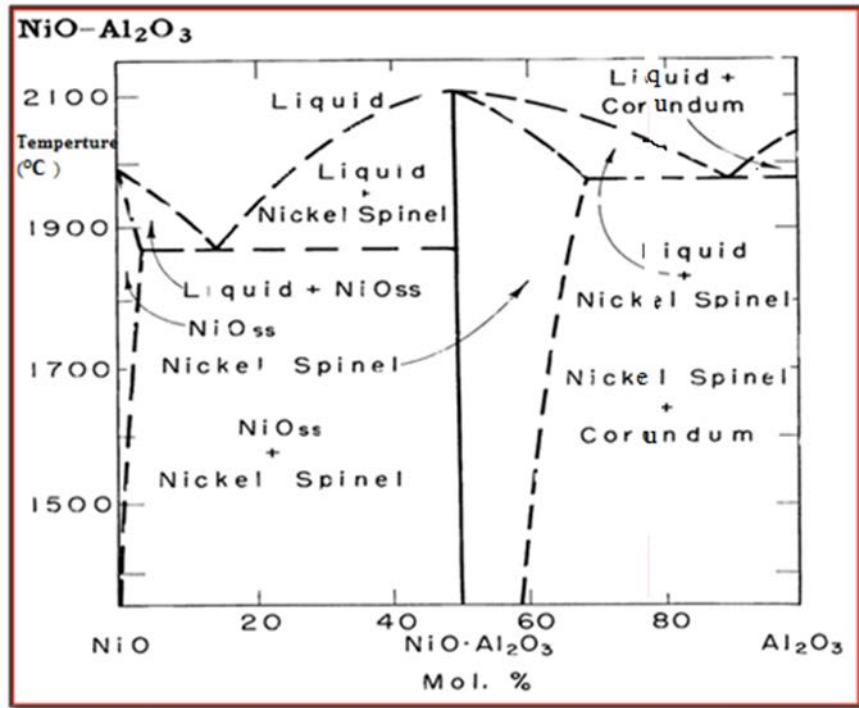


Fig.1 Phase diagram of nickel aluminate (NiAl₂O₄), [Triani R.M, & Bergmann C.P.,(2001)].

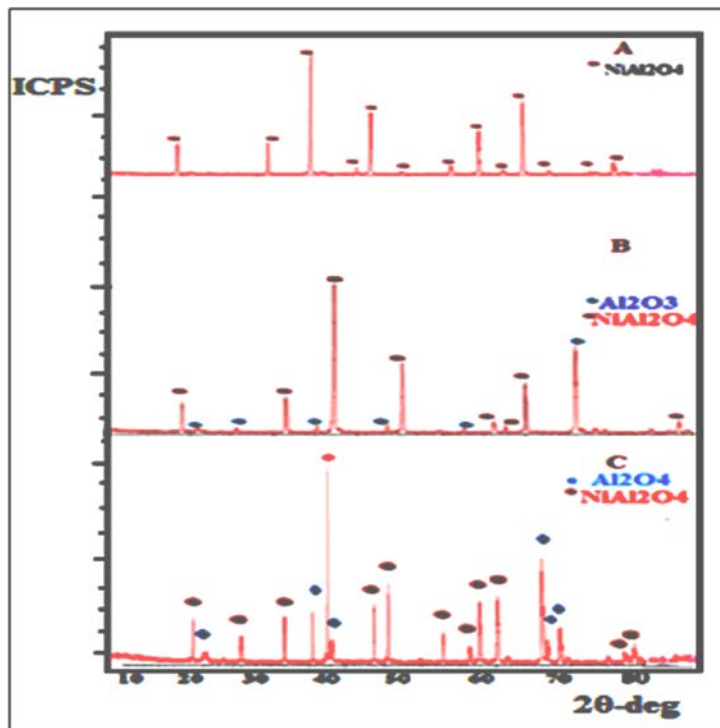


Fig. 2. XRD analysis for different percentage nickel oxide. Where, (a) - 50 wt. %NiO (b) - 30 wt.% NiO and (c) - 20 wt.% NiO.

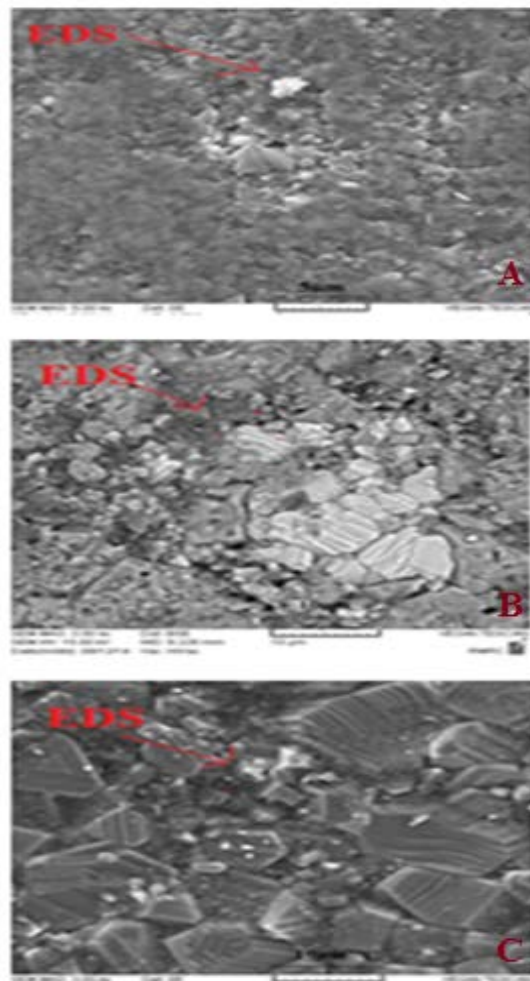


Fig.3 Scanning electron microscopy for nickel aluminate, various percentage and magnification (A1,B1)at 20 wt% NiO, (C1,D1) at 30 wt% NiO and 50 wt % NiO at(E1,F1).

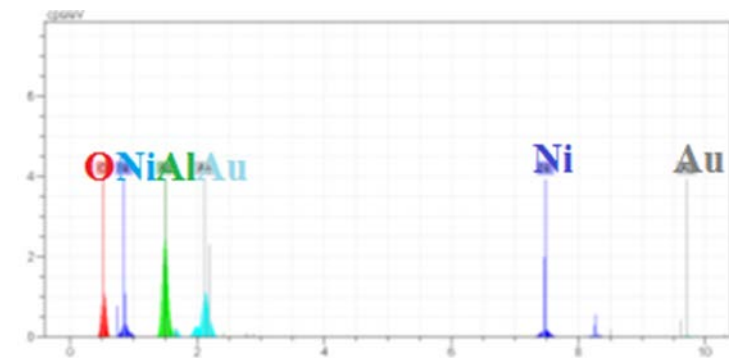


Fig. 4 Energy dispersive X-ray at 20wt% NiO for A image in SEM.

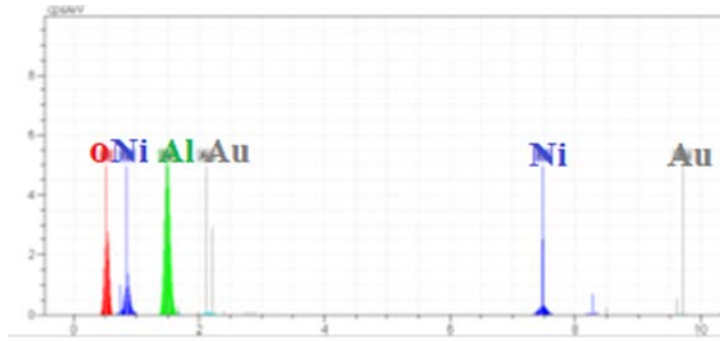


Fig. 5. Energy dispersive X-ray at 30 wt % NiO for B image in SEM.

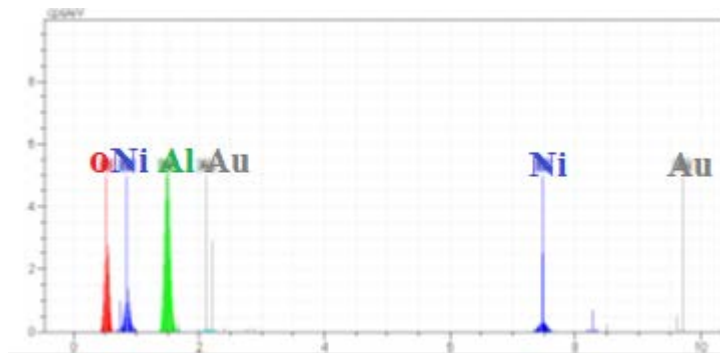


Fig. 6. Energy dispersive X-ray at 50 wt % NiO for C image in SEM.

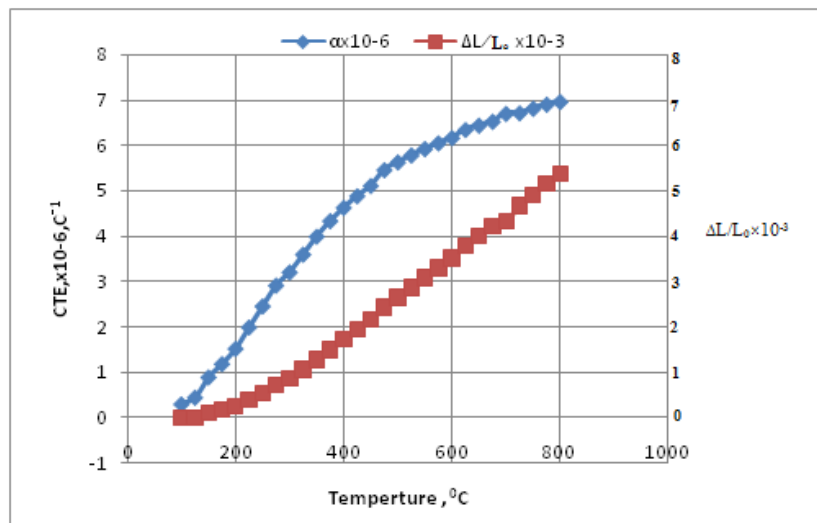


Fig. 7 CTE and change length at 20wt% NiO .

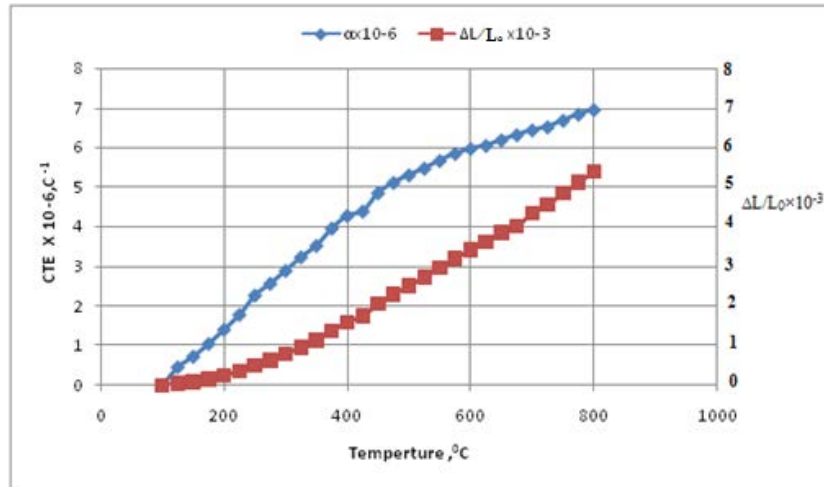


Fig. 8. CTE and change length at 30 wt% NiO .

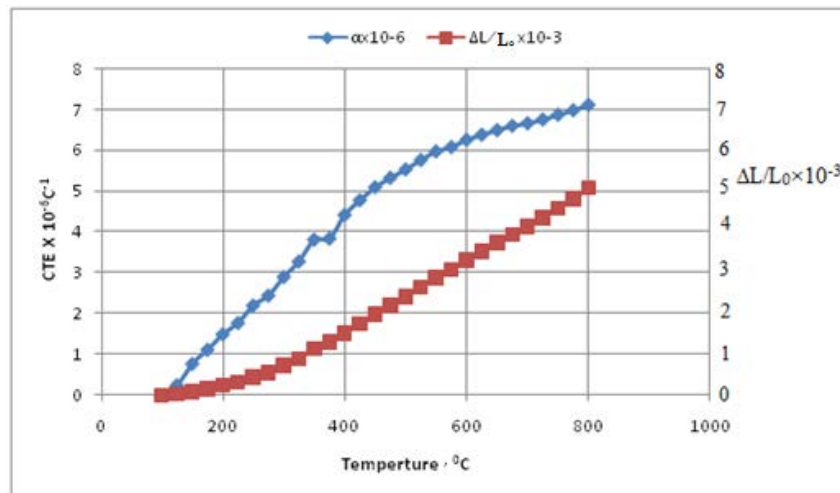


Fig . 9 CTE and length change at 50 wt %NiO.

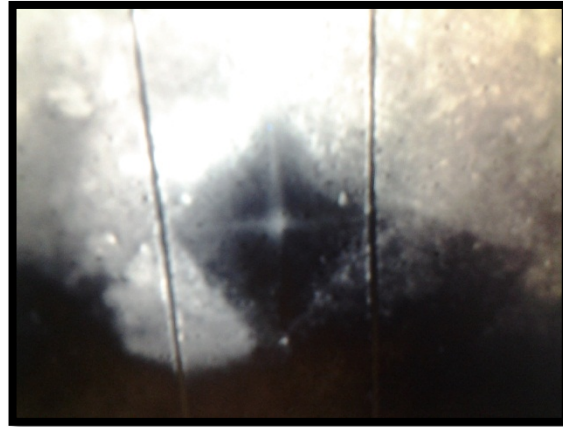


Fig. (10) : Micro-Vickers indentation after thermal shock without cracking at 30wt% NiO at 1200 °C

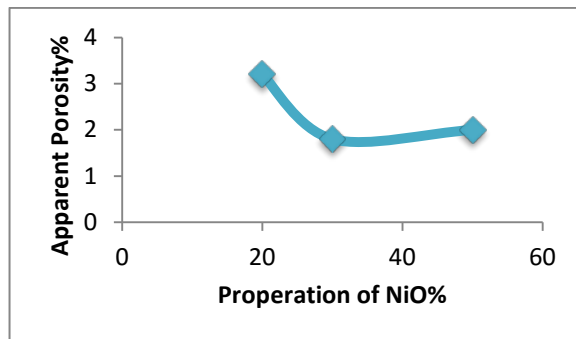


Fig.11. The thermal shock for porosity at 500°C.

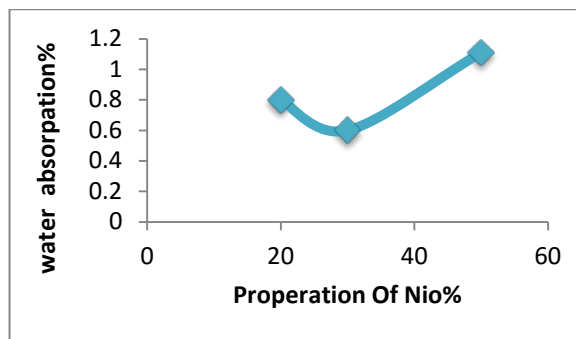


Fig. 12. The result thermal shock for water absorption at 500 °C.

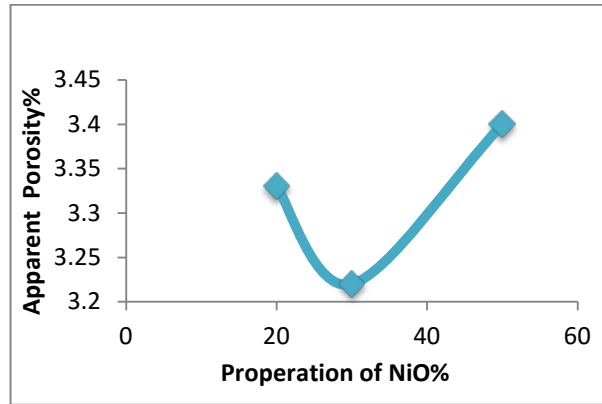


Fig. 13. The result thermal shock for porosity at 1000 °C.

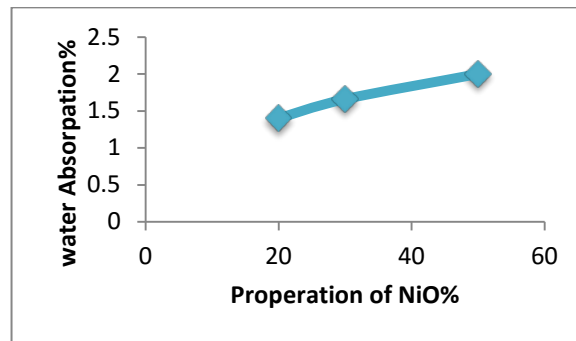


Fig. 14. The result thermal shock for water absorption at 1000 °C.

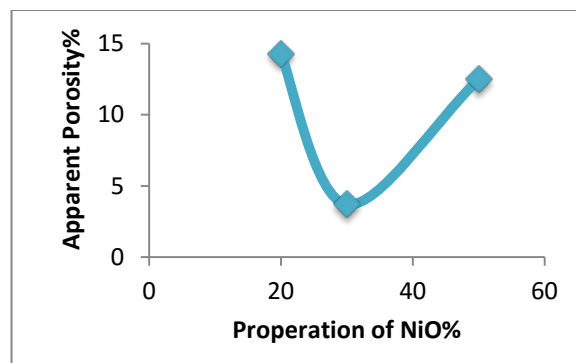


Fig.15. The result thermal shock for porosity at 1200°C.

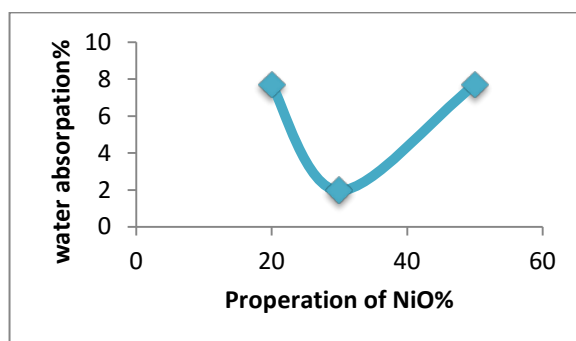


Fig.16. The result thermal shock for water absorption at 1200 °C.

Table 1. XRD data for 20 wt% NiO.

2 θ	I/I ₀	d-(Å)	phases
19.408	21.807	4.571	NiAl ₂ O ₄
21.372	5.4216	4.163	Al ₂ O ₃
26.193	13.253	3.4008	NiAl ₂ O ₄
32.156	22.168	2.785	NiAl ₂ O ₄
35.488	24.096	2.529	Al ₂ O ₃
37.44	100	2.399	NiAl ₂ O ₄
37.996	10.843	2.366	Al ₂ O ₃
43.880	28.915	2.062	NiAl ₂ O ₄
45.488	37.469	1.9930	NiAl ₂ O ₄
52.94	14.457	1.7290	NiAl ₂ O ₄
56.272	8.433	1.633	NiAl ₂ O ₄
57.644	29.518	1.598	NiAl ₂ O ₄
2 θ	I/I ₀	d-(Å)	phases
60	31.855	1.5406	NiAl ₂ O ₄
61.607	3.012	1.5044	Al ₂ O ₃
66.076	50.602	1.4133	Al ₂ O ₃
66.781	11.084	1.4005	Al ₂ O ₃
68.232	16.385	1.374	NiAl ₂ O ₄
78.1928	8.433	1.221	NiAl ₂ O ₄

Table 2. XRD data for 30 wt% NiO.

2θ	I/I_0	$d(\text{\AA})$	<i>phases</i>
19.212	20.481	4.626	NiAl ₂ O ₄
25.876	4.216	3.446	Al ₂ O ₃
31.956	24.096	2.8010	Al ₂ O ₃
35.292	4.939	2.542	NiAl ₂ O ₄
37.056	100	0.635	Al ₂ O ₃
43.528	6.024	2.079	NiAl ₂ O ₄
45.292	46.385	2.000	Al ₂ O ₃
52.696	3.855	1.7368	NiAl ₂ O ₄
56.060	9.036	1.640	Al ₂ O ₃
57.444	6.987	1.603	NiAl ₂ O ₄
59.604	32.530	1.5498	NiAl ₂ O ₄
65.832	56.024	1.390	NiAl ₂ O ₄
69.016	2.530	1.359	Al ₂ O ₃
77.84	9.638	1.226	NiAl ₂ O ₄

Table 3. XRD data for 50 wt. % NiO.

2θ	I/I_0	$d(\text{\AA})$	<i>phases</i>
19.133	26.785	4.640	NiAl ₂ O ₄
31.764	26.190	2.816	NiAl ₂ O ₄
37.056	100	2.426	NiAl ₂ O ₄
43.528	5.952	2.079	NiAl ₂ O ₄
45.096	51.547	2.011	NiAl ₂ O ₄
49.404	3.57	1.845	NiAl ₂ O ₄
55.88	7.738	1.6499	NiAl ₂ O ₄
59.408	36.904	1.554	NiAl ₂ O ₄
62.94	3.571	1.475	NiAl ₂ O ₄
65.488	63.095	1.425	NiAl ₂ O ₄
74.547	4.1666	1.272	NiAl ₂ O ₄
77.644	9.523	1.229	NiAl ₂ O ₄

Table4. Porosity, water absorption and hardness properties before test thermal shock.

Proportion (wt.%)	20	30	50
Porosity%	0.76	1.4	2.17
Water absorption	0.4	0.66	0.95
Hardness	19.96	12.58	30.87

Table 5. porosity and water absorption after thermal shock.

Proportion%	Porosity at 500°C	Porosity at 1000°C	Porosity at 1200°C	Water absorption at 500°C	Water absorption at 1000°C	Water absorption at 1200°C
20	3.2	3.33	14.280	0.8	1.4	7.60
30	1.8	3.22	3.734	0.6	1.66	1.92
50	2.9	3.40	12.570	1.5	2.00	7.66

Table 6. Micro- hardness after thermal shock.

Proportion of NiO%	Micro-hardness 500°C	Micro-hardness 1000°C	Micro-hardness 1200°C
20	12. GPa	9 GPa	1.8 GPa
30	12.GPa	9.4 GPa	4.5 GPa
50	21.25 GPa	12GPa	2.6 GPa

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