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THERMAL EXPANSION OF SOME NICKEL AND COBALT SPINELS AND THEIR SOLID SOLUTIONS

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16. Abstract

Thermal expansion of spinel bars representing the binary systems nickel chromate - cobalt chromate ($NiCr_2O_4$-$CoCr_2O_4$), nickel chromate - nickel aluminate ($NiCr_2O_4$-$NiAl_2O_4$), and cobalt chromate - cobalt aluminate ($CoCr_2O_4$-$CoAl_2O_4$) was measured in the 25° to 1050° C temperature range. The coefficients of thermal expansion were found to have values characteristic of other refractory oxides. $CoCr_2O_4$, $NiCrAlO_4$, and $NiCr_{0.5}Al_{1.5}O_4$ expanded approximately in a linear fashion. $NiCr_{1.5}Al_{0.5}O_4$ had the lowest (4.4×10^{-6}/°C) average coefficient at 500° C, and $Ni_{0.25}Co_{0.75}Cr_2O_4$ (6.9×10^{-6}/°C) at 1000° C. Qualitative observations indicated that chromia-rich spinels exhibited much lower electrical resistivity than spinels containing alumina.

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THERMAL EXPANSION OF SOME NICKEL AND COBALT SPINELS AND THEIR SOLID SOLUTIONS

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SUMMARY

Spinel solid solutions were prepared in the binary systems nickel chromate - cobalt chromate ($NiCr_2O_4$-$CoCr_2O_4$), nickel chromate - nickel aluminate ($NiCr_2O_4$-$NiAl_2O_4$), and cobalt chromate - cobalt aluminate ($CoCr_2O_4$-$CoAl_2O_4$) in intervals of 25 atomic percent. Their thermal expansion was measured from room temperature to about 1050° C with the aid of a cathetometer. The coefficients of thermal expansion were found to have values characteristic of other refractory oxides. $NiCr_{1.5}Al_{0.5}O_4$ had the lowest (4.4×10^{-6}/°C) average coefficient at 500° C and $Ni_{0.25}Co_{0.75}Cr_2O_4$ (6.9×10^{-6}/°C) at 1000° C. $CoCr_2O_4$, $NiCrAlO_4$, and $NiCr_{0.5}Al_{1.5}O_4$ expanded in approximately linear fashion. Qualitative observations on electrical resistivity of spinels revealed that alumina-rich spinels had much higher resistance at room temperature and at 900° C than the chromia-rich ones.

INTRODUCTION

A limiting factor in the use of nickel- and cobalt-base superalloys for high-temperature applications can be spalling of their oxide scales in cyclic operation. It has been shown (refs. 1 and 2) that spinels are one of the constituent phases in the scales which form during oxidation of many superalloys. Because spalling can be related to the thermal expansion characteristics of an oxide scale - metal substrate system, it is of interest to know the coefficients of thermal expansion of spinels and their solid solutions. Although coefficients of thermal expansion for some simple spinels can be found in the literature (refs. 3 and 4), data on their solid solutions are not available.

The objective of this work was to determine coefficients of thermal expansion in the nickel chromate - cobalt chromate ($NiCr_2O_4$-$CoCr_2O_4$), nickel chromate - nickel aluminate ($NiCr_2O_4$-$NiAl_2O_4$), and cobalt chromate - cobalt aluminate ($CoCr_2O_4$-$CoAl_2O_4$)

binary systems. Such spinels are commonly observed during oxidation of Ni- and Co-base superalloys in both the bare and aluminide-coated conditions. Thermal expansion measurements were made on sintered spinel bars from room temperature to about 1050° C in air.

Also, in the course of this work some qualitative observations were made regarding sinterability and electrical resistivity of these spinels.

EXPERIMENTAL PROCEDURE

Sample Preparation

Reagent grade powders of $NiO, CoCO_3, Al_2O_3$, and Cr_2O_3 (table I) were blended in an agate mortar to make compositions in the following binary spinel systems (table II):

$$NiCr_2O_4 - CoCr_2O_4$$
$$NiCr_2O_4 - NiAl_2O_4$$
$$CoCr_2O_4 - CoAl_2O_4$$

A solution of stearic acid in acetone (0.2 g of stearic acid for each composition) was added to each powder mixture, which was stirred under low heat until all acetone evaporated. After this, the powder mixtures impregnated with binder were pressed into 1/4- by 1/4- by 1/4-inch (0.635- by 0.635- by 10.160-cm) bars under 20 000 psi (about 13.8×10^7 N/m^2) pressure and sintered individually to avoid cross contamination. Sintering was performed in air using the following procedure: each bar was placed in the furnace at room temperature and heated in 8 hours to 1500° C, held at this temperature for 24 hours, and cooled down to room temperature in 24 hours. The sintered bars were examined visually for soundness and made into test specimens by grinding manually to the final shape on a recrystallized alumina plate. Because of brittleness some of the bars fractured during grinding, and therefore the specimens varied in length from 6 to 8 centimeters. A top view of the specimen and the experimental setup for thermal expansion measurements is shown in figure 1.

Property Determination

In order to determine whether the synthesis of spinels was complete, a part of each sintered bar was ground in an agate mortar and subjected to X-Ray Diffraction (XRD) analysis. Monochromatic copper Kα radiation and constant XRD operating conditions

(voltage, current, time constant, and scale factor) were used during the whole work. Because $NiCr_2O_4$ at room temperature has a tetragonal structure and undergoes a transformation to cubic structure at about 30° C (ref. 5), its XRD pattern was taken at 50° C.

Thermal expansion of the spinels was measured with a precision cathetometer equipped with a telemicroscope (with standard 90° cross hairs). The measuring range of the cathetometer was 15 centimeters with reading to 0.0001 centimeter. The cross hairs were rotated to form a 45° angle with the horizontal so that during measurements the vertical edges of the sample would dissect the 90° angle. In this manner the effect of cross hair diameter upon the reading was eliminated. The samples were heated in a muffle furnace (see fig. 1) provided with openings for a thermocouple, illumination, and observation. A heat shield placed between the furnace and the cathetometer prevented the heating of the latter. Temperature of the furnace was controlled to within ±5° C. Thermal expansion measurements were made during heating at five different temperatures in the interval from room temperature to 1050° C. In some instances the length determinations were also made on cooling. They were found to be consistent with the measurements obtained during heating (within the limits of experimental error). In general, after cooling to room temperature, the specimens shrank to their original lengths or were somewhat longer but still within the limits of the experimental error. The only exception was $CoAl_2O_4$.

Fifteen minutes after the desired temperature was reached, six to eight length determinations were made. The average of these determinations was used to evaluate ΔL. Deviations from the average values never exceeded 0.0020 centimeter, and this value was used to calculate the precision of the coefficient of thermal expansion α. The results of thermal expansion measurements were plotted as $\Delta L/L_0$ as a function of temperature, where L_0 was the length at room temperature and ΔL the length increment.

After completion of the thermal expansion experiment the same samples were used for determination of their apparent densities by the displacement method. In order to prevent the penetration of water into the pores, the specimens were impregnated with a plastic material. Weighing of the specimens was done before the impregnation step.

In addition, some qualitative observations were made concerning the electrical resistivity of spinels at room temperature and at 900° C in air. To do this, the impregnating plastic was burned out by heating the spinel bars slowly in a muffle furnace to about 900° C. Then one side of each bar was coated with an organic compound of platinum, leaving 1 inch (2.54 cm) in the center uncoated. Subsequently all the bars were heated together to 600° C to decompose the organic compound and form the platinum contact surface. This plating procedure had to be repeated with the more porous bars. A probe with the platinum contact points spaced 3 centimeters and connected to a volt-ohmmeter was used to measure the electrical resistance of the spinel bars at room temperature

and at 900° C. When this qualitative type of test was completed, the platinum coating was removed and the bars were subjected to quantitative chemical analysis.

RESULTS AND DISCUSSION

Quality of Samples

The examination of XRD patterns revealed that the synthesis of all spinel compositions was complete. No diffraction lines due to the component oxides or any other phase were detected. Some weak lines, previously not listed in the literature and detected in the patterns were found to belong to the spinels under consideration. As the lattice parameter changed with composition, the position (2θ) of these lines shifted accordingly. Quantitative chemical analysis indicated that the sintered spinels had nearly nominal compositions (table III). From experimentally determined values of apparent density and calculated values of theoretical density (from XRD data) the relative densities (percent of theoretical) were calculated, and they are shown in the third column of table IV. They range from 37.0 to 81.5 percent. Although these densities are relatively low, it has been established (ref. 6) that porosity is one of the parameters which usually do not have an effect on thermal expansion. The absence of permanent dimensional changes due to additional sintering or deformation during testing was confirmed by the length measurements at room temperature before and after testing. The last column in table IV represents some observations relative to mechanical strength and sinterability of the spinel bars.

Properties of Spinel Compositions

An important observation made during the preparation of the spinel bars was the fact that their synthesis was accompanied by an expansion. Most of the bars were visibly larger after synthesis than before. The calculation of the molecular volumes (MV) of the component oxides and the resulting spinels indeed revealed that the sum of molecular volumes of the component oxides was less than the molecular volume of the resulting spinels:

$$MV_{Me'O} + MV_{Me''_2O_3} < MV_{Me'Me''_2O_4}$$

For example, the formation of $NiCr_2O_4$ from the component oxides is accompanied by a

volume expansion of 8.32 percent, $NiAl_2O_4$ by an expansion of 7.43 percent, $CoCr_2O_4$ by an expansion of 8.03 percent, and $CoAl_2O_4$ by an expansion of 7.73 percent. This phenomenon and the low enthalpy values for some of the spinels (refs. 7 and 8) might be factors which could suppress, at least partially, the formation of spinels in the oxide scale in the presence of compressive stresses. The observed (ref. 2) coexistence of the component oxides and the corresponding spinel seems to support this assumption.

XRD patterns obtained from the synthesized spinels revealed that only the spinel lines were present. This is an indication that the binary systems $NiCr_2O_4$-$CoCr_2O_4$, $NiCr_2O_4$-$NiAl_2O_4$, and $CoCr_2O_4$-$CoAl_2O_4$ formed continuous solid solutions. The lattice parameters of these spinel solid solutions (calculated from the very prominent (844) diffraction line), when plotted as function of composition, varied in a smooth, continuous manner (fig. 2). These lattice parameter data indicated that substitution of aluminum for chromium caused a significant decrease in lattice parameters. The substitution of cobalt for nickel did not result in any important dimensional changes in the spinel cell.

Thermal expansion of the spinels is shown in figures 3 to 5. From these diagrams the average linear coefficients of thermal expansion were calculated for 500° and 1000° C temperatures. They were plotted as a function of composition on three diagrams, representing the three binary spinel systems, as shown in figure 6. The precision of α at 1000° C was calculated to be $\pm 0.47 \times 10^{-6}$ per $^{\circ}$C, while at 500° C it was $\pm 0.94 \times 10^{-6}$ per $^{\circ}$C. Figure 6 shows that the α values for $CoAl_2O_4$ were about 30 percent larger than for the other spinels. Also, there is disagreement between the obtained α for $NiAl_2O_4$ at 500° C and the one reported in the literature (ref. 4). Therefore, in order to explain these differences, thermal expansion of $NiAl_2O_4$ and $CoAl_2O_4$ was determined using the high-temperature XRD technique. The XRD patterns were taken at room temperature, 400°, 800°, and 1200° C, and room temperature (after cooling again). The lattice parameters of spinels at each temperature were evaluated by plotting the values of lattice parameter a_o for high 2θ lines against $\cos^2\theta$ and extrapolating linearly to $\cos^2\theta = 0$ (ref. 9). Thermal expansion of both spinels as determined by XRD technique is shown in figure 7, where $\Delta a_o/a_o$ is plotted as a function of temperature. The corresponding average coefficients of thermal expansion at 500° and 1000° C for $CoAl_2O_4$ were 6.75×10^{-6} and 8.72×10^{-6} per $^{\circ}$C and for $NiAl_2O_4$ were 6.47×10^{-6} and 8.32×10^{-6} per $^{\circ}$C. It is evident that XRD values are in better agreement with the rest of the data than the original ones. The fact that during optical measurements the sample of $CoAl_2O_4$ did not return (on cooling to room temperature) to its original length (unlike other compositions) suggests that some cracks must have formed in it. It also appears that values of α for 500° C quoted in reference 4 are too high. This variance cannot be explained because this reference is a compilation of data without any information about the experimental technique employed. R. K. Kirby in an excellent review paper on thermal expansion of ceramic materials (ref. 6) discussed the question of

discrepancies in the data reported in the literature. According to him, the thermal expansion data for ceramic materials varied on the average by about 10 percent, but variations as large as 40 percent also appeared. It is difficult to judge how much of this variation was due to experimental procedures and how much was due to the history and character of the materials. In general, the thermal expansion data presented in this report are contained in an interval of values characteristic of oxides. It should be noted that substitution of Al for 25 percent of the Cr in $NiCr_2O_4$ and $CoCr_2O_4$ produced a decrease in the average coefficient of thermal expansion at 500° C. This effect is less pronounced at 1000° C. A similar phenomenon was observed when 25 atomic percent of cobalt in $CoCr_2O_4$ was replaced by nickel. The compositions $CoCr_2O_4$, $NiCrAlO_4$, and $NiCr_{0.5}Al_{1.5}O_4$ expanded approximately in a linear fashion in the 25° to 1000° C temperature range. The qualitative determinations of electrical resistivity (the fifth and sixth columns in table IV) indicated clearly that alumina base spinels had much higher electrical resistivity than chromia base spinels. The latter exhibited a typical semiconducting behavior.

The transformation of $NiCr_2O_4$ from the low-temperature tetragonal to the high-temperature cubic structure at about 30° C is accompanied by a very small volume change. This transformation is depressed or eliminated by replacing part of the nickel by cobalt. $Ni_{0.75}Co_{0.25}Cr_2O_4$ is cubic and does not exhibit any transformation phenomenon down to room temperature. Probably other additions to $NiCr_2O_4$ have a similar effect because the tetragonal form of nickel chromate was never detected on oxide scales during oxidation of nickel-base superalloys.

CONCLUDING REMARKS

Although the main purpose of this report was to present thermal expansion data for some nickel- and cobalt-base spinels, the qualitative observations concerning their electrical resistivity were also related. Spinels rich in chromia exhibited semiconducting behavior, whereas alumina-rich spinels behaved more like an insulator. One would expect therefore that the diffusion process would be slower in alumina- than in chromia-rich spinels. This in fact was observed by R. Lindner and Å. Åkerström (refs. 10 and 11), who investigated diffusion processes in spinels. Slower diffusion rates in alumina-rich spinels means that their presence in the oxide scale would hinder oxidation to a much greater degree than the presence of chromia-rich spinels. It appears, therefore,

that addition of aluminum to the alloys and/or coatings should contribute to the oxidation protection.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, October 28, 1970,
129-03.

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TABLE I. - PURITY OF OXIDES USED FOR SYNTHESIS OF SPINELS

Substance	Concentration, wt %
Al_2O_3	99.96
Cr_2O_3	Chemically pure
NiO - Assay as NiO	99.1
Pb	.002
Cu	.010
Co	.046
Fe	.005
Zn	.010
$CoCO_3$ - Assay as Co	47.3
Cu	.001
Pb	.002
Fe	.004
Ni	.20

TABLE II. - BINARY SPINEL SYSTEMS STUDIED

$NiCr_2O_4$ - $CoCr_2O_4$	$NiCr_2O_4$ - $NiAl_2O_4$	$CoCr_2O_4$ - $CoAl_2O_4$
$NiCr_2O_4$	$NiCr_2O_4$	$CoCr_2O_4$
$Ni_{0.75}Co_{0.25}Cr_2O_4$	$NiCr_{1.5}Al_{0.5}O_4$	$CoCr_{1.5}Al_{0.5}O_4$
$Ni_{0.5}Co_{0.5}Cr_2O_4$	$NiCrAlO_4$	$CoCrAlO_4$
$Ni_{0.25}Co_{0.75}Cr_2O_4$	$NiCr_{0.5}Al_{1.5}O_4$	$CoCr_{0.5}Al_{1.5}O_4$
$CoCr_2O_4$	$NiAl_2O_4$	$CoAl_2O_4$

TABLE III. - RESULTS OF QUANTITATIVE ANALYSIS OF SPINELS

Spinel	Calculated nominal metal content, wt %				Metal content determined by chemical analysis, wt %			
	Ni	Co	Cr	Al	Ni	Co	Cr	Al
$NiCr_2O_4$	25.8	----	45.8	----	23.5	----	48.0	----
$Ni_{0.75}Co_{0.25}Cr_2O_4$	19.4	6.5	45.8	----	19.8	6.6	45.4	----
$Ni_{0.5}Co_{0.5}Cr_2O_4$	12.9	13.0	45.8	----	13.3	12.7	45.8	----
$Ni_{0.25}Co_{0.75}Cr_2O_4$	6.5	19.5	45.8	----	7.0	19.3	45.8	----
$CoCr_2O_4$	----	26.0	45.8	----	----	25.0	46.5	----
$CoCr_{1.5}Al_{0.5}O_4$	----	27.5	36.3	6.3	----	26.3	37.0	6.7
$CoCrAlO_4$	----	29.2	25.7	13.3	----	29.7	27.7	11.6
$CoCr_{0.5}Al_{1.5}O_4$	----	31.3	13.7	21.4	----	31.1	14.7	20.6
$CoAl_2O_4$	----	33.3	----	30.5	----	36.1	----	28.6
$NiCr_{1.5}Al_{0.5}O_4$	27.4	----	36.4	6.3	27.6	----	36.2	6.5
$NiCrAlO_4$	29.2	----	25.8	13.4	29.1	----	25.6	13.5
$NiCr_{0.5}Al_{1.5}O_4$	31.6	----	13.7	21.4	33.6	----	14.8	18.8
$NiAl_2O_4$	33.2	----	----	30.6	32.9	----	----	30.8

TABLE IV. - DENSITY AND ELECTRICAL RESISTANCE[a] OF SPINEL SAMPLES

Composition	Theoretical density, g/cc	Relative density, percent of theoretical	Electrical resistance, ohms		Remarks
			At 25° C	At 900° C	
$NiCr_2O_4$	5.23	53.5	$4 \cdot 10^4$	15	Did not sinter well, friable
$Ni_{0.75}Co_{0.25}Cr_2O_4$	5.22	76.2	3×10^4	4	Did not sinter well, friable
$Ni_{0.5}Co_{0.5}Cr_2O_4$	5.22	74.1	10^3	8	Did not sinter well, friable
$Ni_{0.25}Co_{0.75}Cr_2O_4$	5.21	70.3	10^2	8	Did not sinter well, friable
$CoCr_2O_4$	5.22	63.3	Very large[c]	50	Did not sinter well, friable
$CoCr_{1.5}Al_{0.5}O_4$	5.01	37.0[b]	Very large	Large[d]	Did not sinter well, friable
$CoCrAlO_4$	4.81	64.3	Very large	5×10^2	Sintered well, somewhat friable
$CoCr_{0.5}Al_{1.5}O_4$	4.66	62.0	Very large	Large	Sintered well, strong
$CoAl_2O_4$	4.51	81.5	Very large	Very large	Dense and hard
$NiCr_{1.5}Al_{0.5}O_4$	5.07	43.0[b]	10^4	60	Did not sinter well, friable
$NiCrAlO_4$	4.90	68.5	10^3	2×10^2	Sintered well, somewhat friable
$NiCr_{0.5}Al_{1.5}O_4$	4.69	71.2	Very large	5×10^2	Sintered well, strong
$NiAl_2O_4$	4.50	70.5	Very large	Very large	Sintered well, strong

[a]Qualitative estimate only.
[b]Double checked by measuring dimensions and weighing rectangular bars.
[c]Meter set for 1 megohm range did not show any deflection.
[d]Meter set for 1 megohm range moved slightly.

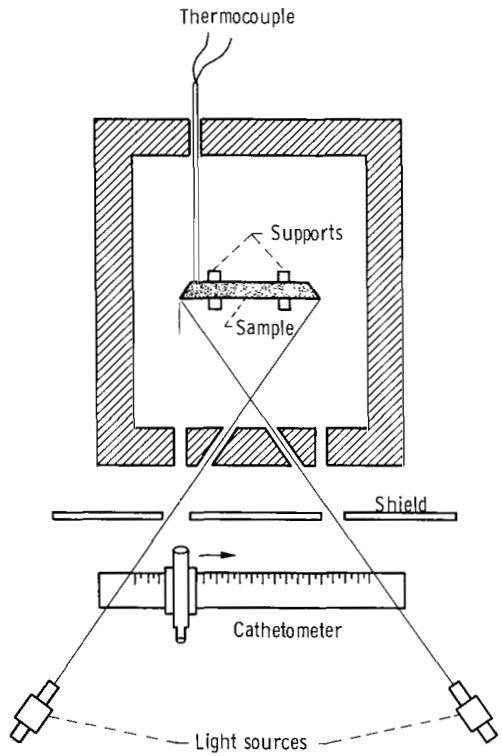

Figure 1. - Schematic representation of experimental setup for measuring thermal expansion.

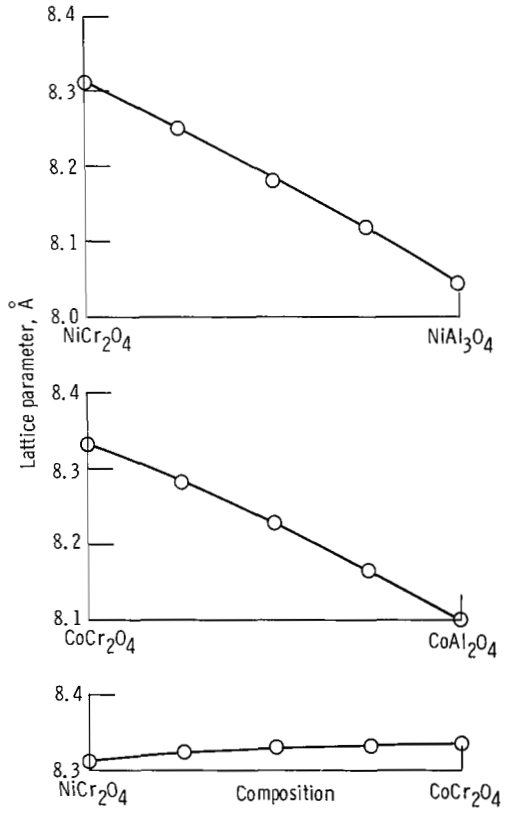

Figure 2. - Lattice parameters of spinels and of their solid solutions.

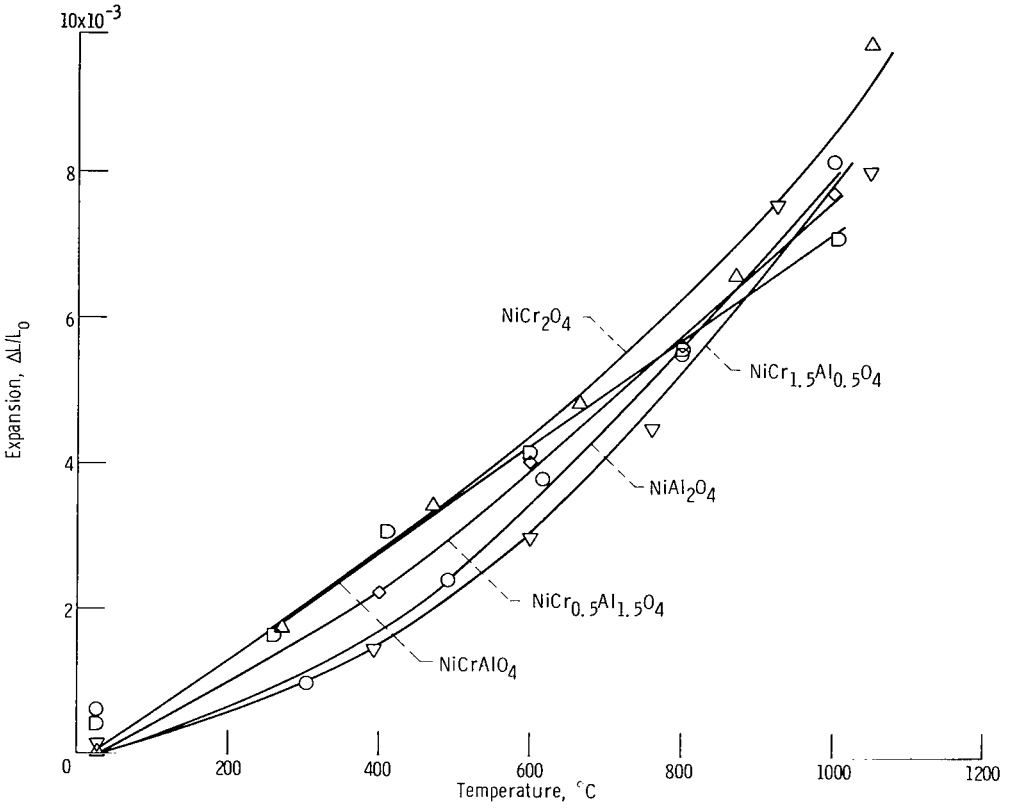

Figure 3. - Thermal expansion of spinels in $NiCr_2O_4$ - $NiAl_2O_4$ system.

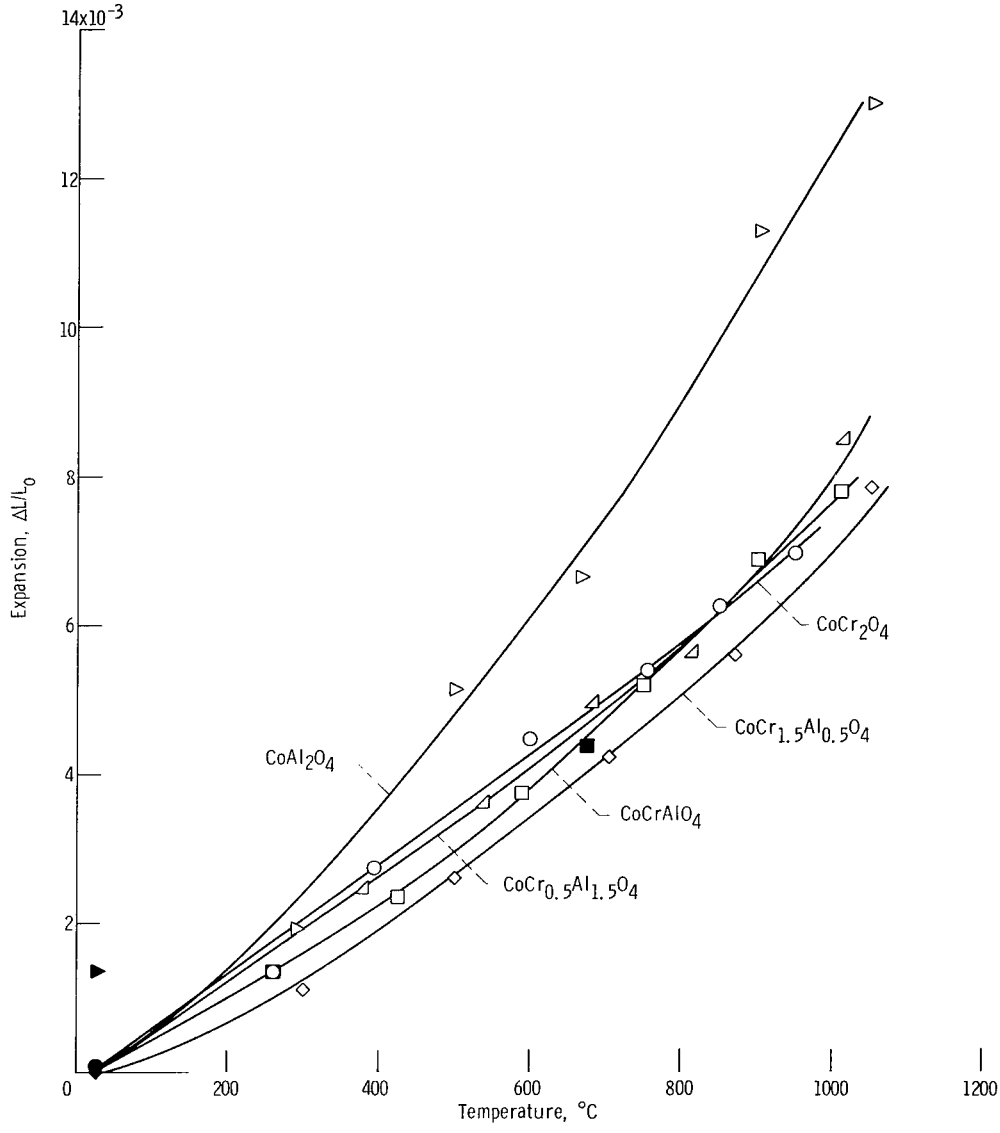

Figure 4. - Thermal expansion of spinels in $CoCr_2O_4$ - $CoAl_2O_4$ system.

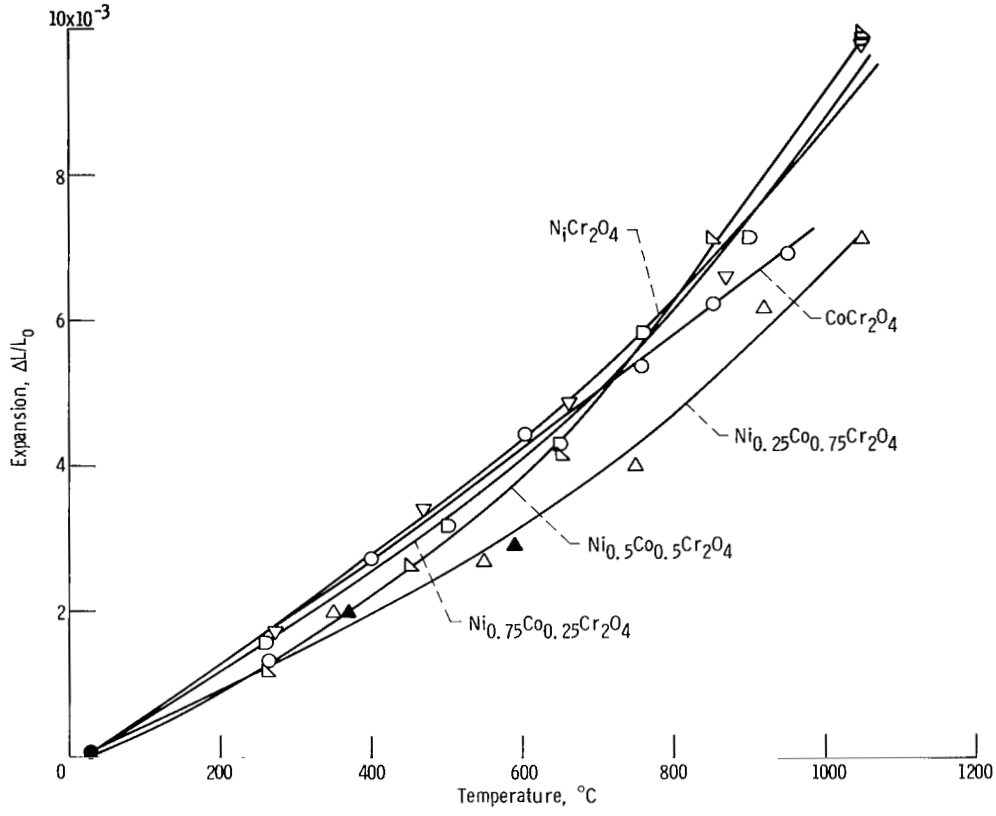

Figure 5. - Thermal expansion of spinels in $NiCr_2O_4$ - $CoCr_2O_4$ system.

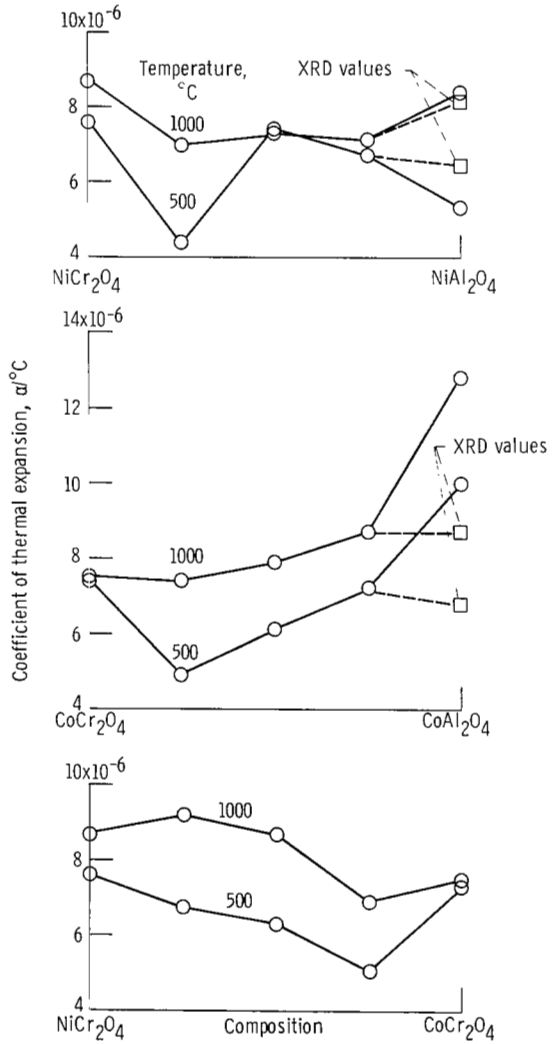

Figure 6. - Average coefficients of thermal expansion at 500° and 1000° C. Values for lattice parameter from reference 7: for $NiO \cdot Al_2O_3$, 7.79×10^{-6} at 25° to 500° C and 8.41×10^{-6} at 25° to 1000° C; for $CoO \cdot Al_2O_3$, 8.00×10^{-6} at 25° to 500° C and 8.52×10^{-6} at 25° to 1000° C.

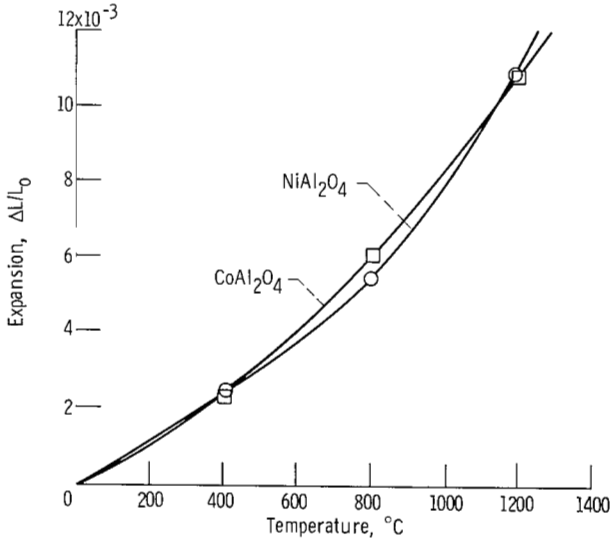

Figure 7. - Thermal expansion of $NiAl_2O_4$ and $CoAl_2O_4$ by XRD method.