High Temperature Physical and Chemical Stability and Oxidation Reaction Kinetics of Ni–Cr Nanoparticles

Md Taibur Rahman, Kathryn Mireles, Juan J. Gomez Chavez, Pui Ching Wo, José Marcial, M. R. Kessler, John McClay, C. V. Ramana, and Rahul Panat

School of Mechanical and Materials Engineering, Washington State University, Pullman, Washington 99163, United States
Department of Mechanical Engineering, University of Texas at El Paso, El Paso, Texas 79968, United States

ABSTRACT: We report on the high temperature oxidation behavior and stability of nickel–chromium (Ni:Cr at 80:20 wt %) alloy nanoparticles (NPs) at temperatures up to 973 K. Structural characterization of the oxidized Ni–Cr NPs provides evidence for the inhomogeneous oxide formation with the presence of NiO, NiCrO4, and Cr2O3 phases, indicating a degradation in the oxidation resistance of Ni–Cr NPs compared to comparable bulk compositions. Chemical identification coupled with thermogravimetric analysis indicates an increase in the activation energy for oxidation reaction from 1.69 to 2.98 eV for conversion ratios of 0.1 to 0.56, respectively. The higher activation energy values compared to those reported for Ni NPs at similar conversion ratios demonstrate the superior oxidation resistance of Ni–Cr NPs compared to Ni NPs. Theoretical modeling of the experimental data suggests that the reaction kinetics were diffusion dominated and could be described by the classical Jander 3D diffusion model. The implications of these experimental data and modeling aspects are discussed to demonstrate the potential of these Ni–Cr NPs for high temperature applications.

1. INTRODUCTION

Nickel–chromium (Ni–Cr) alloys have found widespread use in high temperature applications due to their high melting point (∼1400 °C), high electrical stability with temperature (e.g., low temperature coefficient of resistance, i.e., TCR, of ∼85 ppm/°K), and a high oxidation resistance. For example, the Ni–Cr alloys are one of the oldest known materials used as resistive heating elements. In addition, the bulk Ni–Cr alloys have also been used under ambient conditions when the electrical stability under temperature drifts is important. Recently, environmentally sustainable fabrication methods such as additive manufacturing and printed electronics have necessitated the use of materials in the nanoparticle (NP) form rather than the bulk for device manufacturing. For example, NP-based additive methods have been used to fabricate electronic devices such as biosensors, capacitive touch sensors, antennas, and flexible conductive networks. However, utilization of Ni–Cr NPs in these emerging technologies requires a detailed, fundamental understanding of their oxidation behavior and high-temperature chemical stability. Furthermore, a fundamental understanding of the oxidation behavior of Ni–Cr at the nanoscale is also of interest for their potential applications in catalysis, semiconductor metallization, and the passivation of alloys.

The oxidation behavior of alloys is highly complicated, and the process depends upon the compositions and diffusivities of different species at a given temperature. In the case of bulk Ni–Cr alloys, it is generally recognized that in order to support a predominantly Cr oxide layer at the alloy-scale interface, a minimum Cr content of about 10 wt % is required. The oxide scale in such cases is stable with no evidence of undesirable spinel (NiCr2O4) and only a thin NiO layer present from the time of oxide nucleation. For bulk Ni–Cr alloys with Cr content ≤10 wt %, however, the oxide scale is unstable and consists of micrometer-length-scale layers of an outer zone of NiO, an intermediate zone of NiO containing spinel particles (i.e., NiCr2O4), and an inner region containing Cr2O3 particles embedded in nearly pure Ni. As would be expected, the bulk Ni–Cr alloys with 20 wt % Cr (i.e., the alloy composition chosen for the current study) form a highly stable oxide up to 800–1200 °C.

It is known that at nanoscales the high surface-to-volume ratio of the oxidizing species promotes the inward diffusion of oxygen and outward diffusion of metal ions through the oxide layer, required for the continued oxidation reaction. Although the details of Ni–Cr NP oxidation, and hence its stability, are largely unknown, several recent in situ TEM observations have shed some light on oxidation initiation in Ni–Cr alloys. Initial stages of Ni–9 wt % Cr oxidation using environmental TEM showed a step-by-step adatom growth mechanism in 3D with a nonuniform oxidation due to local surface kinetic variations. Further, it was reported that for Ni–Cr alloys with Cr content lower than about 14 wt % the Cr based oxides could not be detected in the initial oxidation stage.

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while the Cr$_2$O$_3$ phase is always present when Cr concentration is >30 wt %. In other words, the initial oxidation was dominated by the epitaxial growth of NiO rather than Cr oxide. At lower Cr concentration (5 at. %), in situ TEM at 573 K showed different oxidation rates for Ni and Cr, with outward Ni diffusion, giving rise to voids in the alloy NPs. A similar phenomenon consisting of void formation in nanoparticles during oxidation has also been reported for Fe. Note that the oxidation kinetics of nanoparticles can be studied by measuring their precise weight gain as a function of heating rate by standard thermogravimetric analysis (TGA). This data can be used to obtain the activation energies at different conversion ratios. The oxidation mechanisms/kinetics are then identified by comparing the results with standard rate kinetic models. In this context, the fundamental mechanisms of oxide formation and the physical stability of the nanoparticles in the Ni–Cr alloy system are scientifically quite important. In particular, the oxidation kinetics at nanoscales will determine the applicability of the Ni–Cr nanoparticles in various high temperature applications and has not been investigated before. The ultimate goal for the present work, therefore, was to carry out a detailed study of the high temperature oxidation of a commonly used Ni–Cr alloy (with 20 at. % Cr) NPs and determine the structural changes, phases formed, and the oxidation kinetics. Spherical Ni–Cr nanoparticles were subjected to oxidation for up to 973 K in a TGA apparatus to identify the precise weight gain and the oxidation conversion ratio. Transmission electron microscopy (TEM) and selective area electron diffraction (SAED) were used to directly observe the nanoparticles and gain insight into the resultant phases of the formed oxides. The nanoparticles were further analyzed using X-ray diffraction (XRD) for amorphous/crystalline phase identification and to characterize particle coalescence, crystallite sizes, and lattice strain. The activation energies of the oxidation reaction were then calculated at different oxide conversion ratios. Finally, we used this information to identify the active oxidation mechanisms for this alloy.

II. EXPERIMENTS

The Ni–Cr alloy NPs had a composition of Ni:Cr, 80:20 wt %, a spherical shape, an average diameter of about 70 nm, and an oxygen passivation layer around the particles (oxygen content of 3 wt %) from manufacturer specifications. The NPs were subjected to TGA analysis in a Discovery Series thermogravimetric analyzer (TA Instruments, New Castle, DE). The weight of the Ni–Cr alloy NPs used for TGA was $\sim 8.75 \pm 0.15$ mg. The Ni–Cr nanoparticles were placed on a platinum TGA pan with a diameter of 10 mm. All experiments were performed under atmospheric pressure conditions using air as the oxidant. The gas flow rate was set as 20 mL min$^{-1}$ for all the experiments. The experiments were started at room temperature and performed at five different heating rates varying from 5 to 25 K min$^{-1}$ (both included) in steps of 5 K min$^{-1}$. The measurements were stopped upon reaching a temperature of 973 K (set by the TGA pan capability). This temperature was well exceeding the temperature range of interest where electronic chips can survive in high temperature sensor circuits ($\sim 723$ K for the current state-of-the-art wide-band-gap semiconductors such as SiC) but was not enough to complete the nanoparticle oxidation process as confirmed by XRD studies afterward.
The morphology and crystal structures of the samples pre- and post-TGA were examined through imaging and SAED analysis in a TEM (Philips CM200, operating at 200 kV and equipped with a LaB6 filament and a Gatan CCD camera). The TEM samples were prepared by immersing the Ni−Cr nanoparticles (as-received or oxidized) in ethanol and sonicating for 2 min before deposition onto a carbon-coated TEM copper grid. The XRD study on nanoparticles (as-received and oxidized) was carried out at room temperature with a PANalytical X’Pert Pro MPD X-ray diffractometer (PANalytical Inc., EA Almelo, Lelyweg, Netherlands). The XRD used Cu Kα radiation (λ = 1.5406 Å) at 45 kV and 40 mA. Scans were taken in Bragg–Brentano geometry with a 0.05° step size and a 10 s dwell. One scan was taken for a bulk powder sample of the precursor material. For the oxidized samples, 12 scans were summed together in order to increase the signal-to-noise ratio. Lattice parameters and phase ratios were least-squares fit using Rietveld refinement with HighScore Plus software (PANalytical, EA Almelo, Lelyweg, The Netherlands).

III. RESULTS AND DISCUSSION

A. High Temperature Structural and Phase Stability of Ni−Cr Nanoparticles. Transmission Electron Microscopy (TEM). The representative TEM images of the as-received and post-TGA Ni−Cr NPs are shown in Figures 1a and 1b, respectively. The as-received Ni−Cr nanoparticles had a size distribution of ∼77 ± 31 nm. Some outliers (large particles) are also observed. The particle size range was reasonably close to the supplier specification of the mean diameter of 70 nm. The higher magnification image in Figure 1a confirmed the spherical shape of the as-received particles. The particles had a core−shell structure, with the core showing the Ni−Cr alloy and the shell with the oxide passivation (thickness of 3.85 ± 0.48 nm) which was used to prevent NP agglomeration during dispersion according to the supplier. Note that similar oxide passivation (a few nanometers thick shell layer) is observed in other NP systems (e.g., Fe41,42) and prevents agglomeration. The Ni−Cr NPs exposed to 973 K and removed from the TGA (Figure 1b) were approximately equiaxed but not spherical and had Feret diameters (i.e., distance between the two parallel planes restricting an object perpendicular to that direction) ranging from ∼80 to ∼120 nm. These particles also showed a high degree of oxidation (as confirmed by TEM-SAED and XRD). The irregular shape of the oxidized nanoparticles is likely to be the result of a nonuniform oxidation process that occurred along the spherical surface of the as-received NPs as observed from other Ni−Cr systems in the literature.35 This oxidation behavior is completely different compared to bulk Ni−Cr alloys with same composition that show a near ideal Cr2O3 scale formation.27

The SAED patterns of the oxidized and as-received (nonoxidized) nanoparticles obtained in the TEM are shown in Figure 2a and Figures 2b,c, respectively (see Figure S1 for images without annotations). The ring-shaped diffraction patterns in both cases suggest the presence of randomly oriented nanocrystals, which is in agreement with the TEM images shown in Figure 1. The SAED pattern obtained from the nonoxidized sample (Figure 2a) shows strong reflections close to Ni and Ni5Cr. We note that Ni and Ni5Cr share similar crystal structures and lattice parameters, making it difficult to unambiguously differentiate between them. It is, however, very likely that both phases are present given that Ni5Cr has 22.8 wt % of Cr, which is very close, but not equal, to the manufacturer specification on the overall Cr concentration. Half of the SAED pattern obtained from the oxidized sample (Figure 2b) is shown adjacent to that obtained from the nonoxidized sample (Figure 2a) for comparison. In the SAED for the oxidized
sample, strong reflections close to NiO, in addition to Ni and/or Ni$_3$Cr, were observed. Comparing the two SAED patterns obtained from the two samples, there are some stronger reflections along most of the diffraction rings in the oxidized sample. In addition, there are only a few spots for a certain crystal orientation (e.g., only one or two strong reflection spots corresponding to the (002) planes for Ni and Ni$_3$Cr), indicating that the particles are favorably oriented in a certain orientation. The spherical crystals of the as-received NPs (Figure 1a), however, are more likely to be randomly oriented leading to a diffraction pattern that consists of complete reflection rings (Figure 2a). A close examination on the SAED patterns obtained from as-received and oxidized NPs reveals that the diffraction rings exhibit a finite width. This finite width indicates that the lattice parameters have a range of values, which is often observed in nanoparticles due to the relatively larger volume of crystal surface (distortion). Of note, the SAED in Figure 2b did not show any Cr oxides, indicating a dominance of the oxidation of Ni over that of Cr in the nanoparticle system. This behavior is closer to that shown by bulk NiCr alloys with <10 wt % Cr, indicating that the benefit of adding Cr to improve the oxidation resistance of Ni is diminished at nanoscale. In order to further investigate if Cr was oxidized, we obtained SAED patterns from several locations in the oxidized nanoparticles. Figure 2c shows the SAED pattern obtained from an area on an oxidized nanoparticle cluster indicated with a dotted circle in Figure 2d (different location compared to that used to obtain the SAED shown in Figure 2b). Only a small number of diffraction spots are visible in this SAED pattern, suggesting that there are only a small number of crystals within the encircled area. In addition to NiO, this area shows the presence of Ni$_3$CrO$_4$ and Cr$_2$O$_3$, indicating that the Ni–Cr oxidation process consists of reactions involving both of the species and occurs in a nonhomogeneous manner. Nonhomogeneous oxidation (indicated by the segregation of Cr oxide from Ni oxide) was also observed in Ni–5% Cr at nanoscale recently. Interestingly, dislocations (indicated by arrows in the inset of Figure 2d) can be observed from this cluster of particles. The volume of material that contains the dislocation must be a single crystal that is large enough to allow the dislocation structures. Large particles as such are likely to be outliers as observed in Figure 1a or a result of particle agglomeration that formed during high temperature exposure.

X-ray Diffraction (XRD). The XRD patterns of the as-received Ni–Cr NPs and those post-TGA (subjected to the four heating rates of 5, 15, 20, and 25 K min$^{-1}$) are shown in Figure 3. The multiple peaks observed in Figure 3a indicate that the as-received Ni–Cr NPs had a polycrystalline structure and that no oxide phases were detected. For the oxidized samples, the Ni oxide phases appeared for all the heating rates, along with a distortion of the most intense (111) peak as shown in Figure 3b. The database entries used for Rietveld refinement were Ni$_3$Cr (98-010-2820) and NiO (98-024-6910). The XRD was not able to detect any Cr oxide phase, likely due to low concentration of Cr or due to inhomogeneous oxidation, as...
discussed in section A. The lattice constant for pure Ni–Cr NPs from the d-spacing of the most intense peak was 3.5446 Å, in good agreement with that reported previously.\(^\text{[45]}\) Note that the lattice constant is expected to increase due to the sintering/melting of the NPs and the resulting agglomeration during heat treatment. The lattice parameter may also increase due to the ionic radius mismatch between Ni (0.69 Å) and Cr (0.61 Å) along with the diffusion process occurring at high temperature.

Figure 3c shows lattice constants for NPs heated at different heating rates along with the as-received NPs. The lattice constant for post-TGA samples is high compared to that in the as-received condition, with the highest value for the NPs heated at the highest rate (25 K min\(^{-1}\)). Figure 3d shows crystallite size (D) for NPs heated at different heating rates along with the as-received NPs. The crystallite size (D) of the films was evaluated based on Scherer’s formula,\(^\text{[46]}\)

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]  

(1)

where \(\lambda\) is the X-ray wavelength (\(\lambda = 1.5046\) Å), \(\beta\) is the full width at half-maximum (fwhm), and \(\theta\) is the Bragg diffraction angle. The crystallite size increased for the heat treated samples by about 24% (Figure 3d).

B. Thermal Analysis of the Ni–Cr Nanoparticles’ Oxidation Behavior. The weight gain of the NPs due to oxidation was then measured by the TGA technique. These results were combined with the phase identification described in section A to obtain the oxidation conversion ratio for the Ni–Cr NPs at different temperatures. Note that the conversion ratio, \(\alpha\), is the ratio of converted/oxidized fraction, \(x\) of the alloy NPs, to the maximum possible conversion fraction \(x_{\text{max}}\). This can be obtained only by knowing the components of the alloys that have undergone oxidation. The rate of the solid-state reaction, \(\frac{d\alpha}{dt}\), is a linear function of temperature dependent rate constant \(k(T)\) and a temperature-independent function, \(f(\alpha)\), as\(^\text{[39,32,47]}\)

\[
\frac{d\alpha}{dt} = k(T)f(\alpha)
\]  

(2)

The conversion ratio for the TGA measurements is given by the formula

\[
\alpha = \frac{W_r - W_i}{W_f - W_i}
\]  

(3)

where \(W_i\) is the weight at any time, \(t\), \(W_r\) is the initial weight of the specimen, and \(W_f\) is the final weight of the specimen. For nonisothermal/constant heating rate process,\(^\text{[33]}\) eq 2, can be further modified as

\[
\frac{d\alpha}{dT} = \frac{k_0 E_a}{\beta k_B} f(\alpha) e^{E_a/k_B T}
\]  

(4)

where heating rate, \(\beta = dT/dt\), is a constant, \(k_B\) is the Boltzmann constant, and \(k_0\) is the pre-exponential factor. Rearranging the terms of eq 4 and integrating from the initial temperature \(T = T_0\) where oxidation ratio \(\alpha_0 = 0\) to \(T = T_p\) gives\(^\text{[29]}\)

\[
\int_{\alpha_0}^{\alpha_p} \frac{d\alpha}{f(\alpha)} = \frac{k_0 E_a}{\beta k_B} \int_{T_0}^{T_p} e^{E_a/k_B T} dT
\]

\[
= \frac{k_0 E_a}{\beta k_B} \int_{T_0}^{T_p} \frac{\exp(-y)}{y^2} dy
\]

\[
= \frac{k_0 E_a}{\beta k_B} p(y) = g(\alpha)
\]  

(5)

where \(y = E_a/k_B T\) and \(y = E_a/k_B T_p\). The solution of eq 5 can give the activation energy, \(E_a\), at a given conversion ratio, \(\alpha\). Since eq 5 is not solvable analytically, we use three established approaches, namely, the Kissinger method,\(^\text{[48]}\) the Flynn–Wall–Ozawa (FWO) method\(^\text{[49]}\) and the Starink method.\(^\text{[50]}\)

In the Kissinger method,\(^\text{[48]}\) the integral function can be simplified as \(p(y) = \int_{y_0}^{y} \frac{\exp(-y)}{y^2} dy\), and eq 5 can be expressed as

\[
\int_{\alpha_0}^{\alpha_p} \frac{d\alpha}{f(\alpha)} = \ln \left( \frac{k_0 E_a}{\beta k_B} \right) + \ln \left( \frac{1}{\beta y_p} \right) - y_p
\]  

(6)

For a constant fraction transformed, eq 6 simplifies to

\[
\ln \left( \frac{\beta}{T_p^2} \right) = -\frac{E_a}{k_B T_p} + C_1
\]  

(7)

where \(C_1\) is the integral constant

\[
C_1 = \ln \left( \frac{k_0 k_B}{E_a} \right) - \int_0^{\alpha_p} \frac{d\alpha}{f(\alpha)}
\]  

(8)

A plot of \(\ln \left( \frac{\beta}{T_p^2} \right)\) vs \(\frac{1}{T_p}\) for different heating rates can give a straight line having a slope equal to \((E_a/k_B)\), giving the activation energy.

In the FWO method,\(^\text{[51]}\) the integral function is taken as \(\ln \left( \frac{1}{\beta y} \right)\), simplifying eq 5 to

\[
\log(\beta) = -\frac{0.457E_a}{k_B} \left( \frac{1}{T_p} \right) + C_2
\]  

(9)

where \(C_2\) is an integral constant, is

\[
C_2 = \ln \left( \frac{k_0 k_B}{E_a} \right) - \int_0^{\alpha_p} \frac{d\alpha}{f(\alpha)} - 2.315
\]  

(10)

The activation energy can then be obtained by plotting \(\log(\beta)\) vs \(\frac{1}{T_p}\) for different conversion ratios.

Starink\(^\text{[50]}\) has developed a more general expression of \(f(\alpha)\) as

\[
f(\alpha) = (1 - \alpha)^p \left( \ln \frac{1}{1 - \alpha} \right)^q
\]  

(11)

where \(p\) and \(q\) are constants which vary depending upon different reaction kinetics. Considering \(q = 0\) for any homogeneous kinetic reactions, eq 10 can be used to get

\[
\ln \left( \frac{\beta}{T_p^{1.8}} \right) = -\left( \frac{AE_a}{k_B T_p} \right) + C_3
\]  

(12)
where \( C_i \) is the integral constant, \( A = 1.007 - 1.2 \times 10^{-5}E_a \) with \( E_a \), expressed in kJ/mol. The activation energy can be obtained by plotting \( \ln \left( \frac{\alpha}{1 - \alpha} \right) \) vs \( \ln \left( \frac{T}{1/T} \right) \) for different conversion ratios.

**Figure 4** shows the TGA data (weight of the nanoparticles vs temperature) for different heating rates for the Ni–Cr nanoparticles used in this study. The data show an increase in weight of the samples starting at about 275 °C for all heating rates and a similar profile for all the heating rates. The maximum weight gain for the samples is about 18–22% at a conversion ratio of 0.6.

Figure 5 shows the activation energies as a function of the conversion ratio calculated by the three methods mentioned above. The parameters to estimate the activation energies were taken from the thermogravimetric data (Figure 4). The activation energies increased from about 1.7 eV to about 2.9 eV for the conversion ratios of 0.1 and 0.56, respectively. The activation energy profile is similar for all the three approximate methods (within ~1.7%) and is only a function of the conversion ratio. The increasing trend for the activation energy shown in Figure 4 is similar to that seen for the oxidation of the Ni nanoparticles.\(^{29}\) Activation energy for Ni–Cr is higher than that for Ni by about 20–30% for identical respective conversion ratios.\(^{29,31–33,39}\) This data are consistent with the fact that Ni–Cr is known to have higher oxidation resistance in the bulk form when compared to Ni due to a more stable oxide formed by Cr that can impede further oxidation. The increase in the activation energy observed with the conversion ratio seen in Figure 5 can be explained from the fact that the reactants are seen to undergo continuous modifications during oxidation due to factors such as crystal defect formation (dislocations in Figure 2d), particle agglomeration (and hence the surface to volume ratio) (Figures 1b and 2d), and an increase in the crystalline strain (Figure 3c). Also, the particle boundary faces can change to different crystallographic indices during the reaction, and hence the initial reactivity may be different than that for the agglomerated nanoparticles as the reaction progresses.

**C. Reaction Kinetics and Mechanism.** Direct TEM observation and SAED analysis in conjunction with the XRD analysis as described above allow us to identify the reactant phases and gain unprecedented detailed understanding of the oxidation process. In order to determine the reaction kinetics, we fit the experimental data with existing kinetic models.\(^{29}\) The TGA data for 5 K/min heating rate were fitted with different models and plotted in a kinetic “master plot”. The master plot is obtained by plotting \( g(\alpha)/g(\alpha_0) \) as a function \( \alpha \), i.e., by using half-conversion ratio \( (\alpha = 0.5) \) as a reference. The master plots for different solid-state reaction models are summarized by Khawam\(^ {47} \) (see Table 1). For half-conversion ratio, eq 5 can be written as

\[
g(\alpha_0) = \frac{k_p E_a}{\beta k_B} p(y_{\alpha_0}) \tag{12}
\]

where \( y_{\alpha_0} = E_a/k_B T_{\alpha_0} \). Dividing eq 5 by eq 12

\[
g(\alpha) = \frac{p(y)}{p(y_{\alpha_0})} \tag{13}
\]

Next, we plotted \( g(\alpha)/g(\alpha_0) \) as a function of \( \alpha \) for the different oxidation models/mechanisms such as the nucleation model, geometrical contraction model, reaction order models, and diffusion models and compared that with the TGA data shown in Figure 4. Since all the approximations used to solve eq 5 give the activation energies within 1.7%, we will use the FWO method to get \( g(\alpha)/g(\alpha_0) \) and plot the conversion ratio for 5 K min\(^{-1} \) heating rate (the results are the same for other heating rates).

First, we compare our experimental data with the nucleation models, i.e., the solid-state reactions dominated by the nucleation processes such as crystallization,\(^{32}\) crystallographic transition,\(^{33}\) decomposition, etc. The nucleation model assumes constant growth of nucleus without any consideration to growth restrictions which generally expressed as \( g(\alpha) = \alpha^{1/n} \), with \( n = 1, 2, 3, \ldots \) (see Table 1). In real situations, nucleation dominated reactions will encounter two restrictions, namely, ingestion (i.e., existing nucleus growth eliminates nearby
potential nucleation sites) and coalescence (i.e., loss of interface between the reactant and product during the coalescence of the two or more growing nuclei). Avrami\textsuperscript{54} and Erofeyev\textsuperscript{55} incorporated these restrictions into the nucleation models and predicted $g(\alpha) = [-\ln(1 - \alpha)]^{1/n}$, where $n = 1, 2, 3, ...$ (see Table 1). Figure 6a compares $g(\alpha)/g(\alpha_0)$ of the TGA data in the current study with that predicted by the nucleation models. It is clear that the nucleation models cannot predict the observed oxidation behavior of the Ni–Cr nanoparticles. We thus conclude that neither ingestion nor coalescence of nuclei are the dominant factors during the oxidation reaction/kinetics and that the large surface-to-volume ratio offered by the nanoparticles is the key factor in determining the oxidation behavior.

<table>
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Figure 6. Kinetic model fitting for NiCr nanoparticles: (a) nucleation models (A2, A3, A4 represent different Avrami–Erofeyev nucleation models and P2, P3, P4 represent different power law nucleation models), (b) geometry contracting models, (c) reaction order models ($n = 3$–6 represents the order of homogeneous reaction), and (d) diffusion models. Diffusion based 3D classical Jander model fits well with the experimental data.
nanoparticles can make the nucleation process a noncritical factor in determining the oxidation reaction.

Second, we compare the experimental data with different geometry contraction models. These models consider nucleation on the surface of the crystal where the resulting reaction interface progresses toward the crystal center, which controls the rate of the reaction. Depending on crystal shape, geometric contraction models can be two types: (a) contracting area model expressed as $g(\alpha) = [1 - (1 - \alpha)^{1/2}]$; (b) contracting volume model expressed as $g(\alpha) = [1 - (1 - \alpha)^{1/3}]$. However, comparing the experimental data in Figure 6b with the geometry contraction models suggests that these models are not appropriate to describe the reaction kinetics of Ni–Cr nanoparticles. This is not surprising since the oxidation process involves both the ingress of oxygen species and the diffusion of alloy species through the oxide scale.

Next, we consider the homogeneous reaction order models. These models consider reaction rate as proportional to the reactionants fraction remaining raised to a particular power ($n = 1, 2, 3, \ldots$), which is the reaction order. It is clear from Figure 6c that all the homogeneous reaction models do not fit the experimental data particularly well with any $n$th-order homogeneous reaction models. There is significant mismatch between the theoretical and experimental curves. The reason could be that in the case of the current solid-state oxidation reactions the atoms need to permeate the oxide layer to continue the oxidation reaction.

Lastly, we compare the experimental data with surface diffusion models (see Table 1), where the rate of product formation decreases proportionally with the thickness of the product barrier layer. Figure 6d shows that unlike all the previous models, the trends of the master plot for diffusion-based models matches that of the experimental data. For 1-D and 2-D diffusive reaction models, Figure 6d shows only a reasonable fit to the experimental data. The poor agreement is expected considering that the Ni–Cr nanoparticle oxidation process is likely to be 3-dimensional as suggested from TEM images (e.g., Figure 1). We now compare the 3-D diffusion models with the experimental data. Jander developed a 3-D solid-state reaction model, where for a number of particles, $n$, each with a radius $r$, and a reaction zone thickness $x$ (see Figure 7), which will have the conversion ratio as

$$
\alpha = \frac{\frac{4}{3} \pi n r^3 - \frac{4}{3} \pi n r^3 (r - x)^3}{\frac{4}{3} \pi n r^3}
$$

(14)

This equation reduces to

$$
g(\alpha) = [1 - (1 - \alpha)^{1/3}]^2
$$

(15)

From Figure 6d, the 3-D Jander diffusive reaction model provides an excellent fit to the experimental data and is likely to be the dominant reaction kinetic for the oxidation process. This is in spite of the fact that inhomogeneous oxide layer formation was observed, which likely precludes an idealized uniform oxide formation assumed in this model. A second 3-D diffusion-based solid-state reaction model by Ginstling–Brounshtein shows a fit better than the 1-D or 2-D diffusion models but not as good as the Jander model. The Ginstling–Brounshtein model is considered to be important only at high conversion ratios. It is still not clear whether the Ginstling–Brounshtein model will provide the best fit at high conversion ratios (>0.5) or whether some other mechanisms are operative at that level. Because of the distortion in particle shape observed in the current study (Figure 1b and lattice parameters/strain in Figure 3c), there is a question of applicability of the model itself.

On the basis of the results from Figure 6 and the discussions above, we now postulate that microscopic diffusion mechanisms (including transport) to be operating during the Ni–Cr nanoparticle oxidation, while the Jander model does not take into account the diffusion of two species of the alloy. Note that metal oxides generally have ionic bonding, and therefore the oxidation reaction involves the transport of both ions and electrons (ambipolar diffusion in the oxide layer), giving rise to an electric field during oxidation, which influences the diffusion process. A schematic of the possible reaction processes involving the diffusion of Ni and Cr ions and electrons is shown in Figure 8a. If the metal ions have more mobility than oxygen ions, new oxide will form at the oxide interface, while higher mobility oxygen results in new oxide on the oxygen interface. For Ni–Cr alloys, either a monolayer of nichromate (NiCrO₄), separate layers of NiO and Cr₂O₃, or all three phases NiCrO₄, NiO, and Cr₂O₃ can form during oxidation. The TEM SAED patterns clearly show that NiO, NiCrO₄, and Cr₂O₃ were formed due to the thermal oxidation, but in an inhomogeneous manner, with possible epitaxial growth of each of the oxides. The schematic in Figure 8b illustrates the possible evolution of the Ni–Cr alloy nanoparticles during the oxidation processes. We believe that the oxidation reaction progresses with a combined inward diffusion of oxygen and outward diffusion of metal ions through the oxide layer. It is likely that the Cr oxide and Ni oxide form separately and grow epitaxially with metal ions diffusing through the newly formed oxide to reach the surface. The lattice mismatch between the oxides and the alloys can be accommodated by misfit dislocations. As this process continues, the metallic structure eventually converts to metal oxide structure having well-defined grains, with possible agglomeration of adjacent particles.

From the above results, we conclude that the Ni–Cr alloy nanoparticles are stable up to 275 °C, which is significantly lower than the stability temperature for bulk Ni–Cr alloys. For example, at 800 °C, bulk Ni–Cr (80:20) shows a weight gain of only 2.5%, while the equivalent weight gain occurs at ≈400–500 °C for the nanoparticles in Figure 5. Thus, the improvement in the oxidation resistance offered by the addition of Cr to Ni is reduced at nanoscale when compared to bulk alloys. We believe that the minimum Cr proportion in the Ni–Cr alloy nanoparticles required to form a stable oxide layer is higher for nanoparticles than that required for bulk. The degradation of oxidation resistance at nanoscale, however, can
be overcome by sintering the nanoparticles in an inert environment using heat or by photonic flash sintering. Once partly sintered, the nanoparticles will rearrange to reduce the surface to volume ratio and surface curvatures at the nanoscale, and this may result in stable Cr oxides which further retard the oxidation process. Other methods such as promoting the nucleation of a stable oxide layer observed in alumina forming alloys (e.g., NiAl–Cr) needs further work. Additionally, it may be possible to increase the Cr content in the Ni–Cr alloys so that a stable Cr$_2$O$_3$ layer is preferentially formed. A detailed consideration of this phenomenon from the application perspective will be part of a future investigation.

IV. SUMMARY AND CONCLUSIONS

A detailed study of the high temperature physical and chemical stability of Ni–Cr (80:20 wt %) nanoparticles up to 973 K has been performed, and the oxidation mechanisms governing their behavior at nanoscale are reported in this paper. The TEM and SAED analyses showed that the Ni–Cr alloy nanoparticles are heavily oxidized upon exposure to 973 K and form NiO, Cr$_2$O$_3$, and NiCr$_2$O$_4$ as the oxide phases. The oxide formation is inhomogeneous and accompanied by particle agglomeration. The inhomogeneous oxidation behavior of Ni–Cr NPs is different compared to that reported for bulk alloys in the literature where a uniform stable chromium oxide layer is formed. The results suggest a significant degradation of oxidation resistance for these alloys at nanoscale dimension due to the short length scale and high surface-to-volume ratio. XRD analysis of the oxidized nanoparticles showed a 20% increase in the crystallite size and an increase in the lattice constant, suggesting crystal distortion during oxidation. The activation energy increase from 1.69 to 2.98 eV for a conversion ratio of 0.1 to 0.56 suggests the formation of a kinetic barrier to thermal oxidation as the reaction progressed. Comparison of experimental results with existing solid-state reaction models demonstrate that the Ni–Cr oxidation kinetics at nanoscale was 3-D surface diffusion-dominated (rather than nucleation-dominated) and could be described by the classical Jander 3-D diffusion model.

ASSOCIATED CONTENT

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b11560.

Original (unannotated) images of the SAED patterns of the NiCr nanoparticles before and after oxidation (PDF)

AUTHOR INFORMATION

Corresponding Authors
*E-mail rahul.panat@wsu.edu (R.P.).
*E-mail rvchintalapalle@utep.edu (C.V.R.).

ORCID
John McClory: 0000-0001-7476-7771
Rahul Panat: 0000-0002-4824-2936

Notes
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