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ANALYSIS OF RESIDUAL PHASES IN NICKEL ALUMINIDE POWDERS PRODUCED BY REACTION SYNTHESIS

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ABSTRACT

The use of x-ray diffraction has been used to determine phases present after reaction synthesis of Ni_3Al powder. The complex diffraction spectra produced by the powder prompted the development of a simulator. The simulator uses nonlinear regression to determine the weight percent of the phases present. The simulator also determines the broadening of each peak in the spectrum. The phases present in Ni_3Al powder produced by reaction synthesis has been determined with the simulator. The simulator has been used to monitor the progress of phase transformation during various thermal treatments of Ni_3Al powder. A thermal cycle of 1200°C for two hours has been shown to produce a phase-pure product. The activation energy for the interdiffusion of nickel and aluminum has been determined to be 260 ± 35 kJ/mole.

INTRODUCTION

It is the purpose of this paper to describe a method for determining the residual phases in powder produced by reaction synthesis. X-ray diffraction was chosen to determine the phases present after reaction synthesis. Ni_3Al powders produced by reaction synthesis have a multiphase composite microstructure[1]. The phases can have diffraction spectra with very close or overlapping peaks. Some phases present do not have any unique, non overlapping peaks. This makes the diffraction spectra of the powders very difficult to interpret. A simulator was developed to model experimental spectra. With this simulator the phases that are present and the weight percent of each phase can be determined. This method has been applied to monitor the progress of a post heat treatment of Ni_3Al powder. A series of post heat treatments were conducted, the time and temperature dependence of the resulting transformation were determined.

To produce intermetallic powders by reaction synthesis, it is necessary to control the reaction exotherm. Control of the exotherm can be achieved by heat extraction methods. The result of heat extraction is a multiphase, composite product that represents the reaction in a transient condition[2-9]. In many ways the composite powders produced through controlled reaction synthesis are beneficial. If a ductile material is used as a reactant, this component may be preserved in the composite powder structure resulting in a powder that is easily die-pressed. This is advantageous as very often intermetallic powders are too brittle or hard to effectively shape by die compaction. The concentration gradient present in a composite powder also may aid in sintering by providing a diffusive driving force. In thermal spray applications, the lack of phase purity may present problems if a resident phase is lower melting or prone to oxidation. Consequently, it is desirable to determine and control the composition, and phase purity of a reactively sintered powder, tailoring it to the application.

THEORY

The first step in developing the simulator was to chose a model. Using Bragg's Law, the wavelength of the x-ray used, and D-spacings of the compounds, the diffraction angles of each peak can be calculated. Each peak can then be fitted with a gaussian distribution, and all the peaks added up to make a simulated spectrum. The model used for this simulator is then a

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summation of gaussians placed at appropriate angles. The intensity at any angle θ is given by Eq. 1.

$$y(\theta) = \sum_{j=1}^J W_j \sum_{k=1}^{K_j} H_k \exp \left[- \left(\frac{\theta - T_k}{B_k} \right)^2 \right] \quad (1)$$

The parameters H_k , T_k , B_k are: peak height, angle in two-theta, and broadening respectfully. K_j is the number of peaks in phase j . W_j represents the weight percent of phase j , where there are J phases present in the powder. The initial height of each peak, H_k , is determined from the intensity values given in the powder diffraction files. The height of each peak belonging to a particular phase is adjusted by a fractional weight, W_j , this weight can be interpreted as the physical weight percent of that phase present in the powder. The weight of each phase and the broadening of each peak can all be independently varied to match the experimental spectrum. The method used for reducing the error between the simulated and the experimental spectrum was the Levenberg-Marquardt Method for nonlinear regression[10]. This method is advantageous in that it varies smoothly between the inverse Hessian method and the steepest descent method. The latter method is used when the initial guess is far from minimum, and switches smoothly to the former as the minimum is approached. This means that this method will work for both reasonable and unreasonable guesses. Even though this is a robust regression technique, some care has to be taken in selecting the initial guesses. An initial guess with too many phases will lead to long regression times, or incorrect solutions. For accurate regression the initial guess should consist of only the most likely phases.

The method defines a χ^2 merit function

$$\chi^2 = \sum_{i=1}^N \left[\frac{y_i - y(x_i; \mathbf{a})}{\sigma_i} \right]^2 \quad (2)$$

—where $y = y(x_i; \mathbf{a})$ is the model being fitted. The model depends nonlinearly on a set of M parameters $\mathbf{a}$. In this case the set of parameters $\mathbf{a} = \mathbf{H}_k \cup \mathbf{T}_k \cup \mathbf{B}_k \cup \mathbf{W}_j$. The number of parameters $\mathbf{a}$ is consequently three times the number of peaks in the simulation plus the number of phases simulated. Lets say a powder has two phases and each phase has three peaks. This means that the parameter set $\mathbf{a}$ has $3 \times 6 + 2$ or 20 elements. This method has to solve an $N \times N$ matrix, were N is the number parameters being minimized, attempting to minimize all parameters at once can lead to very large matrices. An advantage of the method is the ability to minimize only a subset of the parameters $\mathbf{a}$. This is very helpful in matching diffraction spectra, for example, minimization may be needed on the broadening B_k and not the peak heights H_k Eq. 1. The ability to minimize only a subset of parameters also helps to overcome memory and speed constraints. For spectra with many peaks, memory constraints can be overcome by minimizing only a few parameters at a time. The output of the simulator is the adjusted parameter list $\mathbf{a}$, consisting of: the weight percent of each phase, the height of each peak, the broadening of each peak, the position of each peak, and the background intensity. With this information it may be possible to determine the amount of ordering, and strain in a particular phase. Error bars and a probability of good fit are also available from the simulator.

EXPERIMENTAL

Novamet nickel 123 with a $8\mu\text{m}$ average particle size was mixed to a stoichiometry of Ni_3Al with Valimet H15, $15\mu\text{m}$ average. The powders were reacted using heat extraction methods which yielded the highest percentage of fine particles. The product was milled to $60\mu\text{m}$ average and the resulting powder was examined by x-ray diffraction. The x-ray spectrum was simulated to determine the weight percent of each phase. The x-ray scan was run from 20 to 100 degrees (2θ) in steps of 0.05 degrees, Fig. 1. The simulator covered the same range of 2θ . In order to investigate the homogenization of the powder, samples of the original powder were heat treated at various temperatures, and times. The temperature dependence of the homogenization process

Figure 1: X-ray diffraction scan of powder produced by reaction synthesis with heat extraction methods. Simulator output 0.540 wt.% Ni .190 wt.% Ni_3Al .270 wt.% NiAl

was determined by heat treating samples at temperatures of 900, 950, 1000, 1050, 1100, 1200°C for 2 hours. The time dependence was determined by heat treatments of 0.5, 1, 2, 3, 4, and 5 hours at 1000°C. After the heat treatment the samples were remilled, and x-ray diffraction was performed on each of the samples. The samples were also investigated by electron microscopy to determine the morphology and the phase composition of the fabricated powders. Energy dispersive spectroscopy and back-scattered electron imaging were used to map the compositional variations. The compositional and morphological transformations could be monitored as functions of temperature and time.

ANALYSIS

The diffraction spectrum of the reacted powder, along with the simulated spectrum, can be seen in Fig. 1. There were no aluminum peaks found in the reacted powder, but strong nickel peaks were observed. Other peaks observed in the spectrum correspond to NiAl and Ni_3Al . Nearly all of the Ni_3Al peaks align with the nickel peaks. These peaks can be seen at approximately 44, 52, 76, 93, and 98 degrees. They appear in most cases to be closely spaced doublets, in which the Ni_3Al peaks are the left hand peaks. The Ni_3Al peaks at approximately 35 and 58 degrees are uncharacteristically small due to the fact that the Ni_3Al is still disordered. The rest of the peaks are due to NiAl. The diffraction spectrum of a samples heat treated at 950°C and 1000°C for 2 hours can be seen in Figs. 2 and 3 respectfully. It can be seen that the Ni_3Al peaks grow and that the peaks for nickel and NiAl decrease with increasing temperature. The simulator output shows that the nickel content has decreased to 37 wt% and that the Ni_3Al has increased to 44.5 wt%, for the sample annealed at 1000°C. As can be seen in Table I the amount of residual phases decreases with increasing time and temperature. Complete transformation of the powder to Ni_3Al was achieved with a heat treatment of 1200°C for two hours Fig. 4. This is below the typical sintering temperature for Ni_3Al . Products made by conventional press and sinter techniques will then be phase-pure Ni_3Al following sintering. Plots of the amount of residual nickel vs $\text{time}^{1/2}$ show linear dependence as would be expected from a diffusional type mechanism. The activation energy for this mechanism has been determined to be $260 \pm 35 \text{ kJ/mole}$ [1]. This is consistent results of E.A. Brandes [11].

The microstructure of the reacted powder had two distinct forms. The first is one where

Figure 2: X-ray diffraction of powder after 950°C heat treatment. Simulator output 49.3 wt% Ni 26.0 wt% Ni_3Al 24.7 wt% NiAl .

Figure 3: X-ray diffraction of powder after 1000°C heat treatment. Simulator output 37.0 wt% Ni 44.5 wt% Ni_3Al 18.5 wt% NiAl .

Figure 4: X-ray diffraction of powder after 1200°C heat treatment. Simulator output 0.0 wt% Ni 100 wt% Ni₃Al 0.0 wt% NiAl.

Table I: Simulator output vs time and temperature data

Diffusion Temp. (°C)	Diffusion Time (hr)	Ni	Ni ₃ Al	NiAl
As reacted	—	0.540	.190	.270
900	2	0.533	0.200	0.267
950	2	0.493	0.260	0.247
975	2	0.427	0.360	0.213
1000	2	0.370	0.445	0.185
1025	2	0.277	0.585	0.138
1050	2	0.200	0.700	0.100
1100	2	0.180	0.730	0.090
1200	2	0.000	1.00	0.000
1000	0.5	0.473	0.290	0.237
1000	1	0.413	0.380	0.207
1000	2	0.370	0.445	0.185
1000	3	0.347	0.480	0.173
1000	4	0.300	0.550	0.150
1000	5	0.280	0.580	0.140

the reaction temperature remained below the melting temperature of nickel forming a coated structure. The second is where the reaction temperature reached the melting point of nickel forming a large ligamental structure. Both of these have composite interior structures, consisting of: nickel, nickel with 10 wt% aluminum dissolved in it, Ni_3Al , NiAl , and trace amounts of Al_3Ni_2 [1].

CONCLUSIONS

The developed simulator has been used to determine the residual phases in Ni_3Al produced by reaction synthesis, and used to monitor the phase transformations occurring during thermal treatments of the product. The simulator has also been applied to reaction products of TiAl and Fe_3Al . The simulator is well suited for use where there are many phases present or where phases have similar diffraction spectra. The results of this investigation of Ni_3Al show that homogenization can take place at temperatures below the typical sintering temperature. Two important conclusions can be made from these results. First, compacts pressed from this powder will be homogenized well before the sintering cycle is finished. Secondly, the powder can be homogenized for application that need a phase pure powder. This shows that reaction synthesis can be used to produce powders for both press and sinter applications as well as thermal spray applications.

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