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Sintering of Silica-Nickel Nanocomposites

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Abstract
Nano crystalline metals having sizes of the order of a few nanometers dispersed in silica matrix and the sintering mechanism of the composite have been discussed in this work. Dried silica-nickel nanocomposite gel powders were prepared by acid catalyzed controlled hydrolysis followed by polycondensation of tetraethyl orthosilicate (TEOS) in water-alcohol-Nickel chloride-dextrose solution. The average crystallite size of the metallic Ni particles in the silica matrix is found in the range of 27-60 nm. The powders were pressed and isothermally heat treated over the temperature range of 1100-1250 ^{o}C. Sintering has been delineated to find the mechanical behaviour of silica-nickel nanocomposite.
Keywords: Sol-gel, mechanism, sintering,

I. Introduction

Silica-nickel nanocomposites are important class of powder metallurgy products used in machining applications. There have been many reports on the preparation of ceramic/metal composites such as attrition milling [1] sol-gel [2] ball milling [3] and electroless deposition processes [4].

Among them, the sol-gel process is understood as an excellent method to synthesize the homogeneous ceramic/metal composites [5-6]. It is especially important in the ceramic/metal composites that the metal phase should be controlled with fine sized particles to reduce the formation of cracking, which is due to the mismatch of thermal expansion coefficients between the ceramic and metal phases. Recently, nano ceramics having nano-crystalline grains has been actively investigated [7]. For the preparation of nanocrystalline sintered materials, the conventional sintering technique has been widely used because it has some advantages such as the easy and controlled heating process. Sintering is influenced by several variables. In case of a green compact, which is a multiphase material consisting of at least two phase, namely powder particles and porosity, factors such as the size and shape of the particles as well as those of the pores will influence sintering rate, each in its own way. Time is an important variable in powder metallurgy processing. This typically ranges from 10 minutes to several hours, depending upon the type of powders, its characteristics, size of the component and so on. In the case of powder mixtures, sintering may take place in the presence of liquid phase where the sintering temperature is above the melting point of the low melting constituents [8]. Examples are copper/nickel alloys as well as tungsten carbide and cobalt based tool material. Silica-nickel nanocomposites have taken a place in this group. Sintering requires effective control of heating rate, sintering time, temperature as well as atmosphere for reproducible results. In this study, the silica-nickel nanocomposites powders were synthesized by sol-gel route which were used as a starting material for the sintering process. This work is focused on the interplay between the densification parameters and material properties of silica-nickel nanocomposites depending on the nickel contents and sintering temperature.

II. Experimental

First a set of four gel samples with nickel-chloride and dextrose were synthesized through the following steps. In step 1: 5 cc of tetraethyle orthosilicate (TEOS, 99.8% Merk, Germany) was added with 5 cc of absolute ethanol (99.7%, Zhuhai, China) under constant stirring in a magnetic stirrer at room temperature. In step 2: 5 cc of absolute ethanol and 5 cc of distilled water were mixed under constant stirring. Measured quantity of glucose ($C_6H_{12}O_6$) and nickel chloride ($NiCl_2$) were added to this water-ethanol solution to prepare a homogeneous solution. In step 3: The second solution was added drop wise to the first solution under constant stirring at room temperature. The complete homogeneous mixture consisted of TEOS, $NiCl_2$, glucose, alcohol and distilled water with the ratio of TEOS: alcohol: water as 1:2:1. In step 4: The prepared solution was kept 2-3 days for natural gelling. In step 5: after formation of the gel it was heated at 900 ^{o}C for 8 minutes in nitrogen atmosphere. In Table 1 the composition of the samples undertaken this study was summarized

During heating the chemical reactions occurred throughout the bulk of the matrix are as follows: when the gel is heated at high temperature (900^{o}C) the glucose breaks into carbon and water vapor which again reacts with the carbon to produce in situ hydrogen. This in situ hydrogen reduces Ni^{2+} to Ni^{0} [9,10]. The occurred chemical reactions were as following:

$C_6H_{12}O_6 \rightarrow 6C + 6H_2O$.
$6H_2O + 6C \rightarrow 6CO + 6H_2$.
$NiCl_2 + H_2 \rightarrow Ni + 2HCl$.

Thus metallic nickel particles are formed and as the pores of the silica matrix are in the nano-dimension, this restricts the size of the nickel particles in nanometric order.

We prepare the samples for 5wt%, 10wt%, , 15wt%, , 20wt%, of nickel with 50% excess glucose over that required for the complete reduction of $NiCl_2$. Table 2 summarizes the heat treatment schedules for the $NiCl_2$ containing gel samples.

The heat-treated samples were finely grounded with a mortar pastel. Monochromatic Copper Kα was used to take the x-ray diffraction patterns of the sample with a Rigaku Ultima-III diffractometer.

The XRD analysis of the composite powder samples were given Fig 1 & Fig 2

In order to study the effect of temperature for different compositions of composites at different temperatures, the heat-treated gel powder was pressed uniaxially into a cylindrical disc of diameter 15.0 mm.

The pellets were isothermally heated over the temperature range of 1100 ^oC to 1250 ^oC in a horizontal alumina tube furnace in nitrogen atmosphere for a fixed time of 120 minutes for samples containing different amount of nickel.

To study the effect of holding time, the temperature has been fixed and time has been varied over 30 minutes to 120 minutes.

After sintering the diameter of the pellets are measured. Densification is then calculated by the relative shrinkage given by

$$\text{Densification} = \Delta d/d_i = \frac{(d_i - d_f)}{d_i}$$

where, d_i & d_f stand for the diameter of the cylindrical sample before and after sintering.

III. Results & discussion:

Fig 1 & Fig 2 represent the XRD patterns of the typical gel samples containing 5wt% and 10wt%Ni respectively heat treated at 900 ^oC for 8minutes. Computed d values are in good agreement with standard d values of metallic Ni. Peaks corresponding to metallic Ni are indicated in both figures.

Fig 3 & Fig 4 represents the typical TEM(JEOL JEM 1010) images of the silica - 5 wt% and 10wt%Ni nanocomposite respectively heat treated at 900 ^oC for 8 minutes in N_2 atmosphere. Figures showing the nickel particles of nanometric dimension are clearly visible in the TEM image.

Table 3 contains the densification parameters (Δd/d) as a function of sintering temperature and Fig 5 shows the corresponding graphical representation.

It is observed that as the sintering temperature increases densification occurs due to rearrangement of fine powders of most probably in presence semi liquid nickel. Nickel is in the nanometric dimension. It is expected that semi liquid (liquid like state) will form at lower temperature. Now as temperature increases viscosity decreases which make rearrangement of powder easier & thus densification would be more. This is which is observed from the above figure. The kinetics of sintering is influenced by the temperature and duration of time employed. In order to estimate the effect of time on the sintering of nanocomposites, the samples have been sintered for different periods of time isothermally at 1250 ^oC.

Table 4 contains the densification parameters (Δd/d) as function of time for a fixed temperature at 1250 ^oC and Fig 4 shows the variation of densification as function of time during isothermally sintered at 1250 ^oC

From Table 4 and corresponding Fig. 6 exhibit that for any fixed content of Ni, initially the rate is low followed by slow rate of densification Because to start with prior to formation of liquid, the system is more porous. Thus, the formation of liquid with time increases which causes rearrangement of powder packing by surface tension immediately which is more with higher amount of Ni.

Table 5 and corresponding Fig 7 showing that with increased amount of metal, more of liquid will be available causing more of densification for the same period of time.

IV. Conclusion

The following results were concluded from the experimental findings

1. Silica-Nickel Nanocomposites have been successfully synthesized via sol-gel route through in situ reduction at 900 ^oC for different percentage of nickel.
2. Study of sintering behavior of silica-nickel nanocomposite powders shows that the densification parameter increases with temperature and maximum densification can be obtained at 1250 ^oC for 2 hours and also shows that sintering temperature is the main factor which determines densification.
3. The progress of sintering increases as sintering time increases and reached the highest in 120minutes.

4. The results in Table 5 shows that the densification of silica-nickel nanocomposites at 1250 ^{o}C for 2 hours increases as a function of increasing Nickel content from 5wt% to 20wt%

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Figure Caption:

Figure 1 XRD pattern of sample containing Silica-5wt% Ni heat treated at 900^{o}C for 8 minutes in nitrogen atmosphere.
Figure 2 XRD pattern of sample containing Silica- 10wt% Ni heat treated at 900^{o}C for 8 minutes in nitrogen atmosphere.
Figure 3 TEM image of sample containing silica gel-5 wt% Ni heat treated at 900^{o}C for 8 minutes in nitrogen atmosphere.
Figure 4 TEM image of sample containing Silica gel-10 wt% Ni heat treated at 900^{o}C for 8 minutes in nitrogen atmosphere
Figure 5 Plot of densification parameter as a function sintering temperature
Figure 6 Densification parameters(Δd/d) as function of time for a fixed temperature at 1250^{o}C.
Figure 7 Relationship between Densification parameter and Nickel content.

Table caption

Table 1. Chemical composition of gel samples.
Table 2 Heat treatment schedules.
Table 3 Densification parameter, Δd/d as a function of sintering temperature for a fixed period of time of 120min.
Table 4 Densification parameters(Δd/d) as function of time for a fixed temperature at 1250^{o}C.
Table 5 Densification parameters((Δd/d) as a function of nickel content.

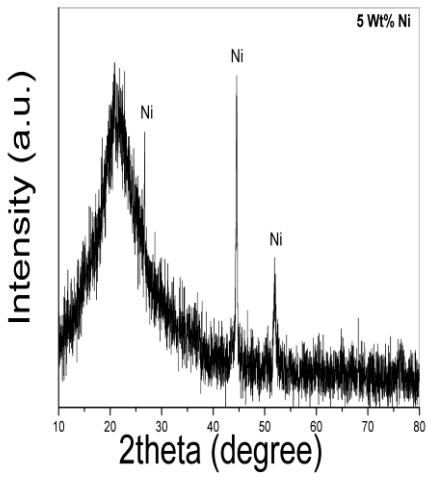
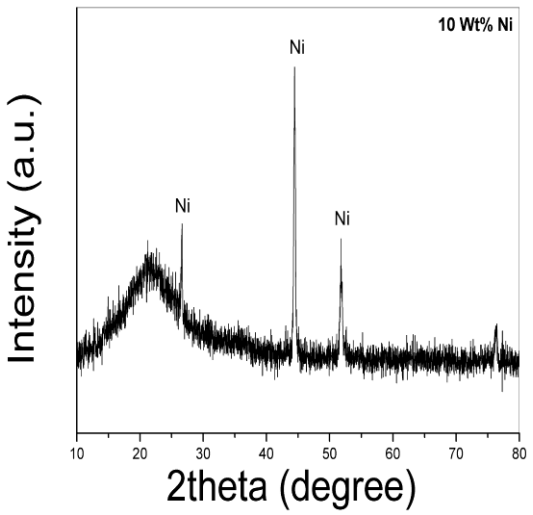


Figure-1



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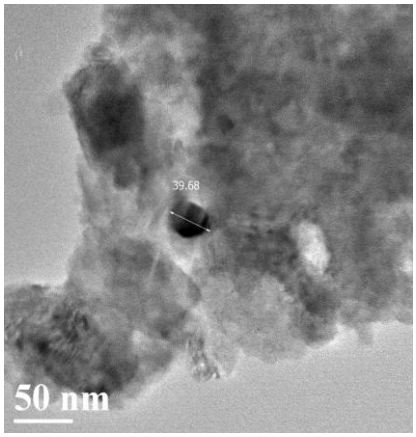

Figure-3

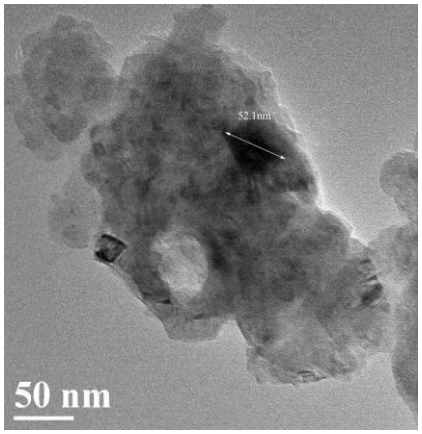

Figure-4

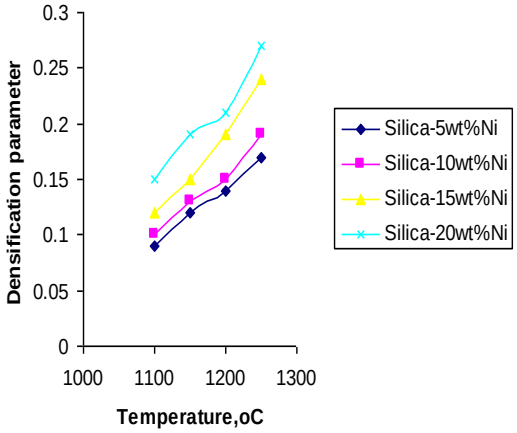

Figure.5

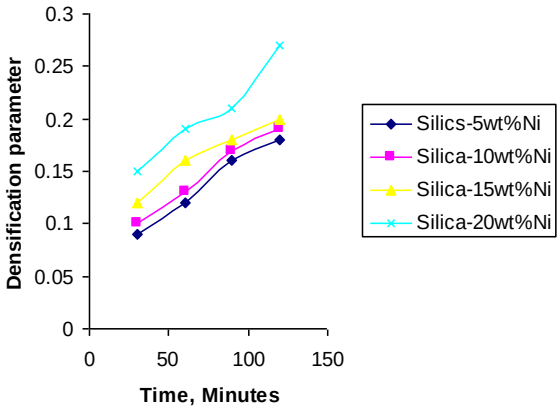

Figure-6

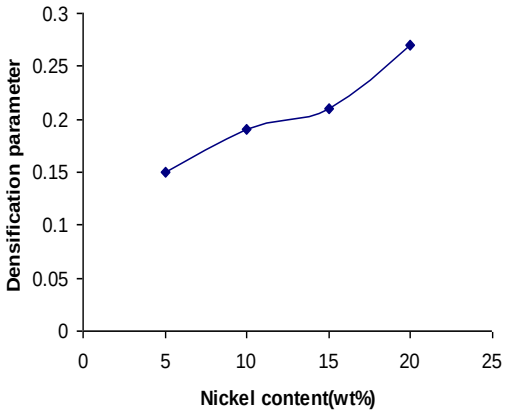

Figure-7

Table-1

Samples	**TEOS: C_2H_5OH:H_2O (By volume)**	**Amt. of $NiCl_2$ (gm)**	**Amt. of Dextrose (gm)**
Silica.5wt% Ni	5cc : 10cc : 5cc (1:2:1)	0.159	0.055
Silica-10wt%Ni	5cc : 10cc : 5cc (1:2:1)	0.318	0.110
Silica-15wt%Ni	5cc : 10cc : 5cc (1:2:1)	0.477	0.165
Silica-20wt%Ni	5cc : 10cc : 5cc (1:2:1)	0.636	0.220

Table-2

Sample	Temperature ^{o}C	Time, minutes	Atmosphere
Silica .5wt% Ni	900	8	N_2 atmosphere
Silica-10 wt%Ni	900	8	N_2 atmosphere
Silica-15wt% Ni	900	8	N_2 atmosphere
Silica-20wt% Ni	900	8	N_2 atmosphere

Table-3

Samples	Densification Parameter,Δd/d			
	1100^{o}C	1150^{o}C	1200^{o}C	1250^{o}C
Silica- 5wt% Nickel	0.09	0.10	0.12	0.15
Silica -10wt% Nickel	0.12	0.13	0.15	0.19
Silica -15wt% Nickel	0.14	0.15	0.19	0.21
Silica -20wt% Nickel	0.17	0.19	0.24	0.27

Table-4

Samples	Densification Parameter,Δd/d			
	30 (minutes)	60 (minutes)	90 (minutes)	120 (minutes)
Silica- 5wt% Nickel	0.10	0.11	0.13	0.15
Silica -10wt%Nickel	0.12	0.14	0.16	0.19
Silica -15wt% Nickel	0.16	0.17	0.18	0.21
Silica -20wt% Nickel	0.18	0.19	0.20	0.27

Table-5

Samples	Densification Parameter,Δd/d
Silica - 5wt% Nickel	0.15
Silica -10wt% Nickel	0.19
Silica -15wt% Nickel	0.21
Silica -20wt% Nickel	0.27