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## Dilatometry of Ball Milled Nickel Nano Powder during Non-Isothermal Sintering

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### Abstract:

*This work attempts to evaluate the sintering mechanisms of ball milled nanocrystalline nickel during nonisothermal heating. Samples showed a sintered density of 91.2% (theoretical) and grain growth up to 414 nm at 1273K. The activation energies of 12.4, 32.0 and 51.6 kJ/mol were found for viscous flow, lattice diffusion and grain boundary diffusion mechanisms respectively. Sintering was found to be controlled by interface reactions involving surface and grain boundary diffusions.*

**Keywords:** Sintering; Dilatometry; Diffusion; Grain growth.

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### Introduction

When a nano powder is sintered, grain growth also occurs concurrently and hence the grain size dependent parameters, such as diffusivities and activation energies continuously change [1-3]. The mass flow mechanism, such as, grain rotations and grain slidings, which are not normally observed in normal powder, were found operative during nano sintering [4, 5]. A number of studies were reported on sintering and grain growth of nanocrystalline nickel (n-Ni) powder. Andrievski [4] reported the formation of non uniform microscopic pores during sintering of n-Ni, which after pilling up, led to particle sliding and rearrangement. Ragulya and Skorokhod [6] employed a rate controlled sintering technique on n-Ni to achieve a density level up to 99% and with a final grain size less than 100 nm. However, no work was reported about the activation energy of sintering and sintering mechanism of n-Ni powder during non-isothermal heating, which is the focus of the present study.

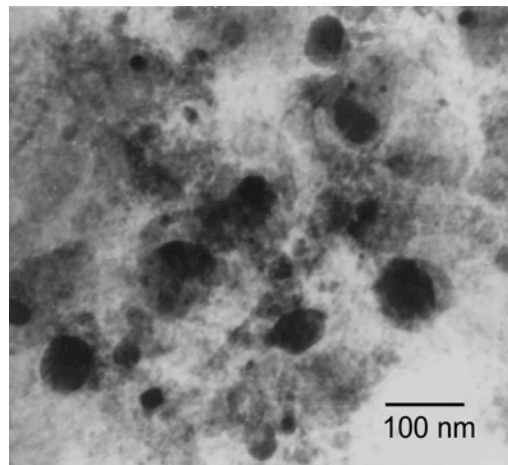
### Experimental

The n-Ni was prepared by high energy ball milling from -325 mesh high purity (99.7%) nickel powder. The ball to powder ratio (weight) was 10:1 using WC balls (~10 mm diameter) and vial (250 ml), with rotating speed of 300 rpm, milling was done for 35 hours on a Fritsch P6 planetary mono mill (Germany). Toluene was used to avoid agglomeration or

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clogging of powders during milling. Average grain size (crystallite size) was found to be 42 nm, calculated through the x-ray diffraction (XRD) analysis [7]. The transmission electron microscopy study of the milled powder revealed, that the particles were in the range of 30 to 60 nm in size (Fig. 1).

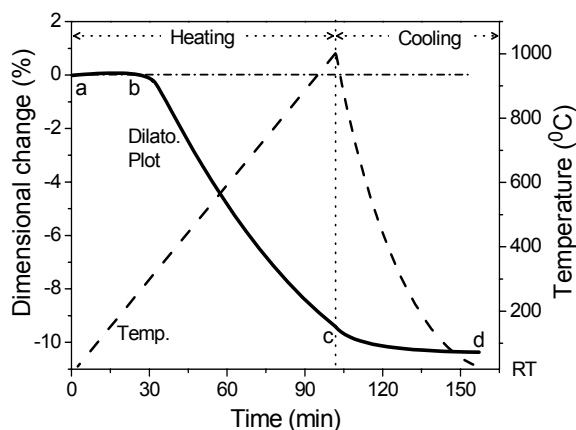


**Fig. 1** TEM micrograph of the 35 h milled Ni powder.

The powder was compacted in a steel die (7.94 mm diameter) by applying uniaxial compaction pressure of about 250 MPa. The  $L_0/d_0$  ratio (where  $d_0$  is the diameter) of the green compact was about 0.55 and the average density of about 5.8 g/cm<sup>3</sup> (~65% theoretical). Sintering of the compacts was carried out in a high sensitivity ( $\pm 0.5 \mu\text{m}$ ) dilatometric system (Shimadzu DT30 Thermal Analyzer, Japan) under high purity argon [further purified by passing through heated (1273 K) titanium turnings]. Compacts were heated with a heating rate of 10°C/min to various temperatures (up to 1273 K). As soon as the temperature reached the set point, the furnace was switched off (without isothermal holding) and the sample was allowed to cool in the furnace. The dimensional changes (in the axial direction) through-out the thermal cycle were recorded continuously on a strip chart recorder. The sintered samples were characterized by XRD for grain size analysis.

## Results and discussion

A dilatometric plot of the sample heated up to 1000°C is shown in Fig. 2. When the heating started, the sintering line moved almost horizontally (a-b) and at about 200°C, it started shrinking which was followed by a rapid shrinkage.



**Fig. 2** Dilatometric sintering curve of the n-Ni powder compact.

It seems that the onset of sintering started at a much lower temperature (below 200°C), which counter acted against the expected thermal expansion effect. When the furnace was switched-off, it showed continuous contraction (c-d). Most of the samples showed nearly isotropic shrinkage. The sintered density was found to increase gradually with temperature and it reached 91.2% (theoretical) at 1273 K (Fig. 3). The grain size grew up to 414 nm at 1273 K (Fig. 3), almost 10 times of the initial size.

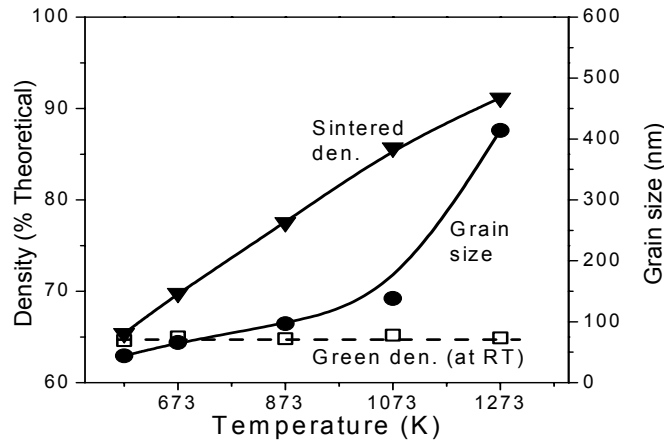


Fig. 3 Sintered density and grain size as a function of temperature, (RT: Room Temperature).

The activation energy (Q) was estimated using equation (1) for densification during a constant heating rate, as reported by Han et al.[8] based on Young and Cutler's [9] equation.

$$\ln\left(T^P \frac{dY}{dT}\right) = -\frac{Q}{(n+1)RT} + \ln C \tag{1}$$

where Y is  $\Delta L/L_0$ ,  $L_0$  is the initial length of the green compact,  $\Delta L$  is the change in length, T is the temperature, R is the universal gas constant, C is a constant depending on material parameters, n and P are constants. P has the value of 1 for viscous flow (VF), 3/2 for VD and 5/3 for GBD. The values of n are 0, 1 and 2 for VF, VD and GBD respectively. Fig. 4 shows the Arrhenius plot of equation (1) to obtain Q. The measured Q for sintering was found to be very low compared to the Q of their self diffusion for a polycrystalline sample, as shown in Tab. I.

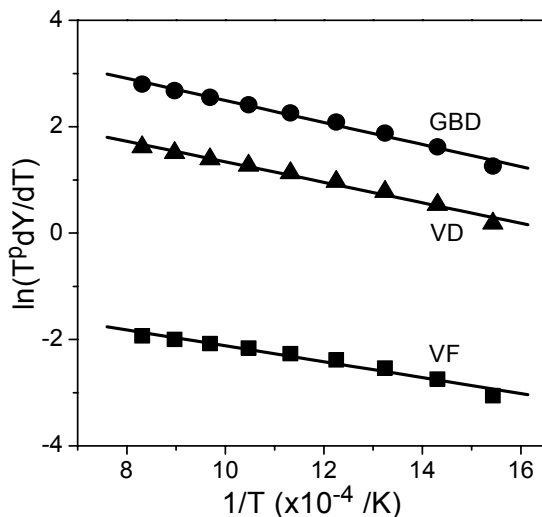


Fig. 4 Arrhenius plots to estimate activation energies for different mechanisms: VF- viscous flow, VD- volume (lattice) diffusion and GBD- grain boundary diffusion.

When the particles are in the nano metric range, it contains two types of grain boundaries: (a) nano grain boundaries and (b) the boundaries of nano grain clusters. It was reported [11] that in nickel, diffusion along nanograin boundaries did not differ from that of grain boundaries in an ordinary sized polycrystal, whereas nanograins cluster boundary diffusion was close to the surface diffusion, which yielded a very low value of Q (Tab. I).

**Tab. I** Calculated activation energies

Mechanism	Q (kJ/mol) of Sintering (in present work)	Q (kJ/mol) for self diffusion (reported for Ni)
Viscous flow	12.4	N.A.
Lattice diffusion	32.0	271.0 (for polycrystalline Ni [10])
Grain boundary diffusion	51.6	115.0 (for polycrystalline Ni [10])
Grain boundary diffusion and surface diffusion	-	46.0 (for nano Ni [11])

However, the observed Q in this work could not be explained by the diffusional process alone. It appears that in the ball milled powder which is likely to have a large amount of dislocations which might be the contribution in densification through inhalation and grain rotations. However, a quantitative analysis of dislocation led shrinkage could not be made in this work, which needs further study. Thus, the sintering of nano nickel is governed by complex interface reactions involving surface and grain boundary diffusions, dislocation motions and grain coarsening.

## Conclusions

Sintering behaviour of n-Ni powder was studied through dilatometry during nonisothermal heating. It showed a low onset temperature of sintering and the activation energies were found to vary from 12.4 to 51.6 kJ/mol. The sintering process was controlled by complex interface reactions.

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## References

1. J. R. Groza, R. J. Dowding, *Nanostruct. Mater.*, 7 (1996) 749.
2. B. B. Panigrahi, M. M. Godkhindi, K. Das, P. G. Mukunda, V. V. Dabhade, P. Ramakrishnan, *J. Mater. Res.*, 20 (2005) 827.
3. Q. Jiang, S. H. Zhang, J. C. Li, *Solid State Comm.*, 130 (2004) 581.
4. R. A. Andrievski, *Int. J. Powder Metall.*, 30 (1994) 59.

5. G. S. A. M. Theunissen, A. J. A. Winnubst, A. J. Burggraaf, J. Eur. Ceram. Soc., 11 (1993) 315.
6. V. Ragulya, V. V. Skorokhod, Nanostruct. Mater., 5 (1995) 835.
7. T. H. D. Keijser, J. I. Langford, E. J. Mittemeijer, A. B. P. Vogles, J. Appl. Crystallogr., 15 (1982) 308.
8. J. Han, A. M. R. Senos, P. Q. Mantas., J. Eur. Ceram. Soc., 19 (1999) 1003.
9. W. S. Young, I. B. Cutler, J. Am. Ceram. Soc., 53 (1970) 659.
10. F. B. Swinkels, M. F. Ashby, Acta Mater., 29 (1981) 259.
11. B. S. Bokstein, H. D. Brose, L. I. Trusov, T. P. Khvostantseva, Nanostruct. Mater., 6 (1995) 873.

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**Садржај:** У овом раду направљен је покушај процене механизма синтеровања млевеног нанокристалног никла током неизотермског загревања. Узорци су имали синтеровану густину од 91.2% (теоријске) и раст зрна до 414 нм на 1273 К. Енергије активације од 12.4, 32.0 и 51.6 кЈ/мол су одређене за механизме вискозног ток, површинске дифузије и дифузије по границама зрна. Нађено је да синтеровање контролишу површинске рекације које укључују површинску дифузију и дифузију на граници зрна.

**Кључне речи:** Синтеровање, дилатометрија, дифузија, раст зрна.

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