Abstract

The sintering mechanisms for nano size powders have not been well-understood and different mechanisms have been proposed by different investigators. In the present work efforts have been made to focus on these issues with special reference to sintering of attrition milled titanium nano particles. Various approaches have been followed to determine the dominant mechanism of sintering. Effect of addition of fast diffusive elements such as nickel on the sintering behaviour of titanium powders has also been investigated.

High purity micron size titanium (mTi) powder (~3-5μm) was used in this study. The nanocrystalline (nTi) powders (~30 nm) were prepared by high-energy attrition milling of micron size powder under a controlled atmosphere. Uniaxially compressed cylindrical samples (~70% theoretical density) of micron size and nanocrystalline powders were sintered in a high sensitivity dilatometer (TMA) over a wide range of temperature (573 K to 1523 K) under high purity inert atmosphere.

The nanocrystalline titanium powders show a relatively low onset temperature and high sintering rate. Sintering in both nano and microcrystalline powders samples result in similar final density (~82 to 83%) at 1250°C). Shrinkage caused due to the particle rearrangements in nano powder could be seen during TMA analysis in the temperature range of 300-450°C. Clear breaks in the sintering data at about 850-900°C in case of mTi samples and 700-800°C in case of nTi samples were observed, indicating a change in sintering kinetics in those two temperature ranges. mTi powders yield an activation energy (Q) of ~184 kJ/mol at low temperature range (≤1148 K) and it reduces significantly in the higher temperature range to ~113 kJ/mol. In the nTi powders Q decreases to extremely low values, 76 to 84 kJ/mol and 60 to 64 kJ/mol at low temperature (≤973 K) and at higher temperature range respectively. It is important to note that the value of Q obtained for mTi powders only at low temperature range, lies in the range of activation energy for titanium self diffusion and rest of observed values are much below the Q of Ti self diffusion. This leads to difficulties in identifying the dominant sintering mechanisms. Hence, the data has been further analysed through the sintering diagram model of Ashby (1974).

Through a detailed analysis of sintering diagram approach, it was found that in the micron size titanium, two lattice diffusion mechanisms (both, from surface source and grain boundary source) are the operating mechanisms. Nanocrystalline titanium shows a continuous change in sintering mechanisms at various stages. Initially sintering starts with

lattice diffusion from dislocations, followed by grain boundary diffusion up to ~973K. At higher temperature volume diffusion mechanism of stage-3 dominates the process.

Stability of the grain size in nano titanium has been observed up to 700°C, which is attributed to the pinning forces arising from impurities (~2wt%) and pores at triple or more particle junctions. At higher temperatures, increased solubility and diffusivity could cause rapid grain growth. The activation energy for grain growth (~63 kJal/mol) has been found to be similar to that of the activation energy of sintering (of nTi). Nano Ti samples showed anisotropy in shrinkage at higher temperatures, which is attributed to a possible high temperature creep.

The addition of ultrafine nickel in small quantities (2 and 5 at%) has been found beneficial in sintering of titanium powders. The addition of nickel does not change the sintering mechanisms of respective powders, but it enhances the sintering rates and drops the activation energy significantly. On the other hand, it also reveals that nickel could be a favourable alloying element for titanium powders for increasing densification rates.

This dissertation is divided into seven chapters. The first chapter contains a general introduction about the importance of the work and the specific objectives of the present investigation. Chapter 2 deals with a detailed literature review, which has been focused in three different areas. This starts with the fundamentals of the sintering, sintering mechanisms and a numbers of sintering models have been described. Next section deals with the general properties nanocrystalline materials and about the sintering behaviour of nano powders. Titanium and its properties such as solubilites, diffusivities and sintering of titanium powders, have been discussed in the last section. The experimental procedures including powder synthesis, characterization, compaction and sintering methods have been explained in chapter three. Chapter four comprises of the observations and results obtained through various experimental. The analysis of the observed sintering data through the classical sintering models has been presented in fifth chapter. The explanations of the experimental results and results predicted through sintering models have been discussed in sixth chapter. The conclusions drawn from the present research have been presented in the last chapter. Finally, the list of references and an appendix containing tabulated data of predicted sintering rates, have been included at the end of the thesis.