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Effect of titania addition on hot hardness of UO_2

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Abstract

Large grain UO_2 is a potential fuel for LWR's for achieving extended burn up. Large grains are obtained by addition of dopants like Nb_2O_5, TiO_2, Cr_2O_3, V_2O_5 etc. However, presence of such dopants might affect the thermophysical and thermomechanical properties of the fuel. In the present investigation the effect of TiO_2 addition on the hot hardness (H) of sintered UO_2 fuel has been studied from ambient to 1573 K in vacuum. TiO_2 content was varied from 0.01 to 0.15 w/o resulting in a grain size (G) variation of 9 to 94 μm. With increase in grain size (or TiO_2 content) H first decreases, attains a minima and then increases further. The increase is more prominent at lower temperature (<773 K) than that at higher temperatures. H vs. $G^{-1/2}$ plots indicates the same type of variation like other oxide ceramics with H minima at an intermediate grain size at low temperature. The intrinsic hardness and softening coefficient of UO_2 indicate cubic dependence on TiO_2 content.

1. Introduction

Large grained UO_2 fuel has been developed as a high burn up fuel for LWRs. The large grain size increases the path length of the fission gas species for transportation to grain boundaries for coalescence and subsequent release. This helps in retention of the fission gases in the matrix without swelling. Though large grain size UO_2 pellet can be obtained by modifying powder characteristic and by increasing the sintering temperature and time, they are commercially not viable and are normally obtained by addition of dopants like Nb_2O_5, TiO_2, Cr_2O_3, and V_2O_5 etc., which also act as sintering aids. The grain size of UO_2 in the final sintered product, however, depends on the type and amount of dopants added.

One of the prerequisites for addition of these dopants to the fuel is that they should not impair any other properties of the fuel. Literatures reveal the effect of Nb_2O_5 [1–5], TiO_2 [2,5–8], Cr_2O_3 [5,9] and V_2O_5 [2] on the sintering behaviour of UO_2 and their effects on other properties. It has been reported [7] that titania addition increases both grain sizes and thermal conductivity of UO_2 by about 10–15%. However, its effect on other material properties, particularly the hot hardness has not yet been ascertained. In the present investigation attempts have been made to study the effect of TiO_2 on the hot hardness of sintered UO_2 fuel. This has been achieved by hardness measurements of UO_2 pellets from ambient to 1573 K in vacuum for titania content varying from 0.01 w/o TiO_2 to 0.15 w/o which resulted in grain size variation from 9.5 μm for UO_2 with 0.01 w/o to 94 μm for UO_2 with 0.15 w/o TiO_2. The grain size of the pure UO_2 pellet (control pellet) was of 9 μm under the same sintering condition.

2. Experimental

2.1. Material

Sintered pellet samples of UO_2 (with and without TiO_2 addition) were made following the conventional

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powder metallurgy method. In this method, UO_2 powders were mixed with the desired quantity of high purity titania powders and dry milled for two hours in a planetary ball mill. The powder mixture was subsequently wet milled for 2 h in ethyl alcohol media for obtaining uniform distribution of titania in UO_2. The ethanol was evaporated in a flat bed under flowing air. The dried powder mixtures were cold compacted at 320 MPa to make the green pellets which were sintered at 1650 °C (1923 K) for 4 h in $Ar + 8\%H_2$ atmosphere. Samples of UO_2 and UO_2 containing 0.01, 0.05, 0.10, 0.13 and 0.15 w/o TiO_2 were prepared. The sintered density of the pellets of about 7 mm in height and 5 mm in diameter were found to be 93–94%TD.

2.2. Equipment

A high temperature microhardness tester (Model: QM, make: M/s. Nikon, Japan) having a load capacity of 50–1000 g, was used for measurement of hot hardness. The equipment uses a microVicker's diamond pyramid indenter in vacuum ($\sim 7\times10^{-3}$ Pa) and is capable of measuring hardness from ambient to 1673 K (maximum). The unique feature of the equipment is that the indenter and the sample are heated in separate furnaces before indentations are made on the sample. The indentation diagonals are measured at the experimental temperature through a microscope and CCTV. The detail description of the equipment has been given in Ref. [10].

2.3. Procedure

Sintered pellets of UO_2 and UO_2 containing TiO_2 were prepared for metallographic examination by mounting, grinding, polishing and etching. The grain sizes of the pellets were measured by the linear intercept method. The pellets were subsequently recovered from the mount and loaded into the sample holder of the hot hardness tester. The accuracy of the hardness tester was estimated by measuring room temperature hardness on copper standards (NBS SRM 1894) at different loads. Room temperature hardness data measured on standard copper samples was within ±5% of the data reported by National Bureau of Standard, USA. Moreover, literature data [11] of hardness of UO_2 (with 14% porosity) was found to be 480 Kg/mm^2 at 1 Kg load and 642 Kg/mm^2 (with 0% porosity) at 25 g load. Hardness data of UO_2 (with 6–7% porosity) of this study is found to be 500 Kg/mm^2 at 1 Kg load, which is in good agreement with the literature value taking into account the variation in porosity factor. Hardness measurements of all the above samples were subsequently carried out at temperatures from ambient to 1573 K in steps of 100 K in a vacuum of 7×10^{-3} Pa. A load of 1000 g was applied for each measurement for a dwell time of 5 s. At each temperature at least 3–4 indentations were made at various locations of the sample. The diagonals of each indentation were measured using a semi automatic telecomparator system. The average of all these diagonals was used to obtain the average hardness at each temperature.

3. Results and discussions

Photomicrographs of UO_2 and UO_2 containing TiO_2 (0.01–0.15 w/o) are shown in Fig. 1(a)–(f) respectively. The photomicrographs indicate presence of equiaxed grains increasing in size with TiO_2 content with intragranular spherical pores of different sizes. No precipitates of UO_2–TiO_2 eutectic [6] for UO_2 containing 0.15% TiO_2 could however be revealed by optical microscopy at grain boundaries (solubility limit TiO_2 at 1650 °C in H_2 atmosphere is 0.13 w/o). Fig. 1(g) shows a typical Vicker's indentation made at 1573 K for the sample containing 0.13 w/o TiO_2 having a grain size of 80 μm.

Fig. 2 shows the sigmoidal pattern of the variation of the grain size with TiO_2 content. Fig. 3(a)–(c) shows the plot of hardness vs. inverse square root of grain size at three different temperature ranges and Fig. 4 shows the plot of hardness vs. temperature for different grain sizes. It should be noted that grain size as well as TiO_2 content influence hardness value at any temperature and also they are interrelated. However, the results have been discussed into three categories signifying the effect of TiO_2 content, grain size and temperature.

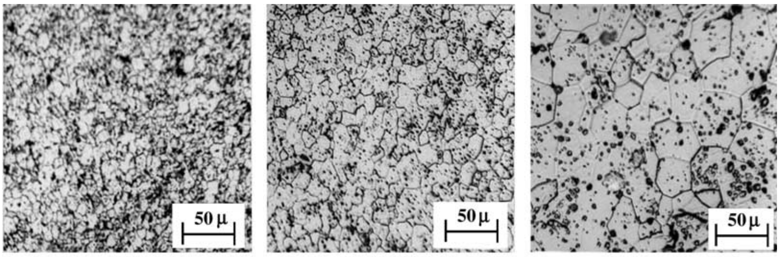
The effect of TiO_2 content, grain size and temperature on hardness and their complex interrelationship could be explained as follows.

3.1. Effect of TiO_2

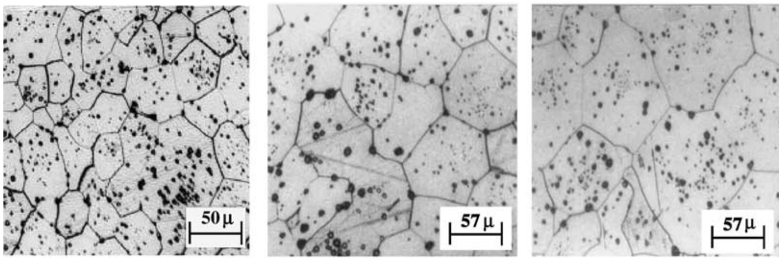
Hardness of UO_2 increases with increase in TiO_2 content at any temperature and hence, the fuel becomes less and less plastic although grain size increases many folds e.g. 9 μm to 94 μm. This increase in hardness could be attributed to solid solution hardening by increasing amount of lattice strain induced by more and more TiO_2 addition within the solubility range. The hardening effect could also be attributed to the hindrance of the dislocation motion by pinning due to the presence of TiO_2 solute atom in UO_2 or precipitates (at high TiO_2 content, low temperature condition).

3.2. Effect of grain size

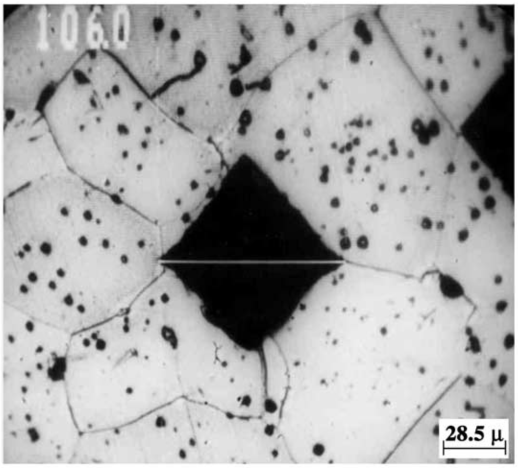
It is very difficult to separate the effect of grain size and TiO_2 content on hardness since the grain size and TiO_2 content are interrelated. However, in order to ascertain the dependence of hardness (H) variation with grain size (G) at various temperatures (T), hardness was



(a) Pure UO_2, $G = 9\mu$ (b) 0.01 w/o TiO_2, $G = 9.5\mu$ (c) 0.05 w/o TiO_2, $G = 18\mu$



(d) 0.10 w/o TiO_2, $G = 60\mu$ (e) 0.13 w/o TiO_2, $G = 80\mu$ (f) 0.15 w/o TiO_2, $G = 94\mu$



(g) 0.13 w/o TiO_2, $G = 80\mu$

Fig. 1. (a–f) Photomicrographs of sintered UO_2 pellets with different TiO_2 content and (g) typical Vicker's indentation obtained at 1300 °C.

plotted as a function of inverse square root of G (based on Hall–Petch relationship), in accordance with a survey made by Rice et al. [12]. The plot of H vs. $G^{-1/2}$ (Fig. 3(a)) shows the same trend like most of the oxide and non-oxide ceramic materials at room temperature i.e. with increasing grain size hardness first decreases, attains a minima and then increases. However, the same trend was not observed at higher temperature and in the present study the whole temperature range has been divided into three regions, namely lower temperature ($T \leqslant 773$ K), intermediate temperature (773 K $< T \leqslant$ 1273 K) and high temperature ($T > 1273$ K) region to discuss their effects on hardness.

At lower temperatures ($T \leqslant 773$ K) hardness decreases sharply with decrease in grain size (Fig. 3(a)), because of two reasons. Firstly, the diagonal length of indentation becomes comparable to that of grain size (i.e. G/D ratio ≈ 1) causing grain boundary spalling due to intergranular crack generation. This results in decrease in hardness [12]. The tendency of spalling is often enhanced by the presence of porosity on grain boundary. Secondly, the lower grain size contains lower amount of TiO_2, which in turn reduces the hardness. These two factors together oppose the strengthening effect due to grain fineness (following Hall–Petch relation) and become predominant. Further decease in grain

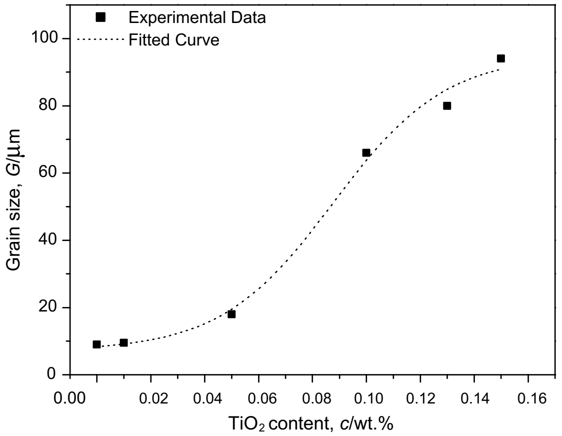


Fig. 2. Variation of grain size, G with TiO_2 content showing sigmoidal nature (up to content of 0.15 wt%).

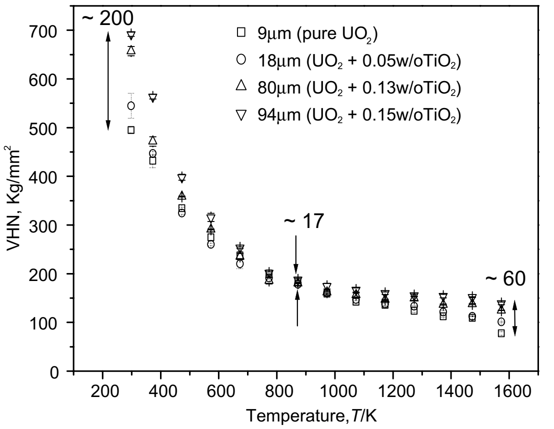


Fig. 4. Plot of hardness as a function of temperature. The vertical lines show the standard deviations.

size increases the hardness due to the effect of grain fineness over spalling. Hence a minimum H value is observed due to transition from grain boundary spalling domination to grain fineness domination. It has been observed that in the lower temperature range there is increase in hardness for the sample with grain size of 9.5 μm (UO_2 +0.01 w/o TiO_2) than that for 9 μm (pure UO_2), which is due to the addition of TiO_2 alone; since the grain size effect is negligible (Fig. 3(a)). Hence hardness data corresponding to 9 μm grain size has not been considered for the fit.

At intermediate temperature range (773 K $< T \leqslant$ 1273 K) the higher grain size shows similar trend in hardness (as observed at lower temperatures) with the exception that the slope is less due to less grain boundary spalling. However, at lower grain size, hardness does not increase as sharply as in case of lower temperature range. With decreasing grain size, on the contrary, it becomes almost independent of grain size (Fig. 3(b)). This could be attributed to lowering of grain boundary strength at this temperature range. Hence, the dislocation piled up stresses generated during indentation is released easily which, in turn, lowers the hardness. As the grain size dependency of hardness at lower grain size is not predominant at this temperature range, H minima is not much pronounced here (Fig. 3(b)).

In the higher temperature range ($T >$ 1273 K), higher grain size shows similar effect as mentioned above. However, with decrease in grain size, hardness gradually decreases. This is attributed to grain boundary sliding which becomes operative at high temperature. Accordingly, smaller the grain size, more weak it becomes, though, the decrease in hardness with respect to grain size is not much (Fig. 3(c)).

3.3. Effect of temperature

Fig. 4 shows variation of hardness with temperature for different TiO_2 content. The spread in hardness data is maximum at 298 K (~200 VHN) and minimum at 873 K (~17 VHN); whereas at 1573 K it is ~60 VHN.

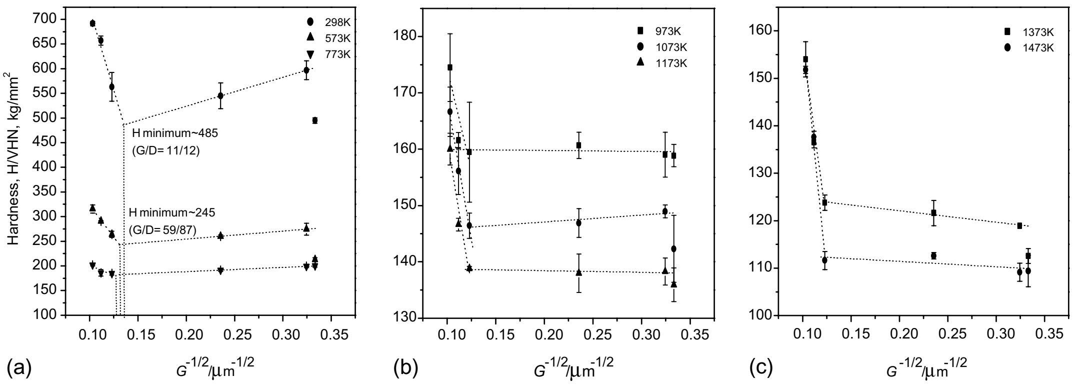


Fig. 3. (a–c) Variation in hardness as a function of $1/\sqrt{G}$ at three different temperature zones. Fitted lines are indicated by dotted line.

The relation between hardness and temperature is given by [13,14]

$$H = A\exp(-BT), \qquad (1)$$

where H is Vicker's hardness, A is the extrapolated hardness value at 0 K (called intrinsic hardness) and B is the softening coefficient of the material. The values of A and B are dependent on the amount of additives or

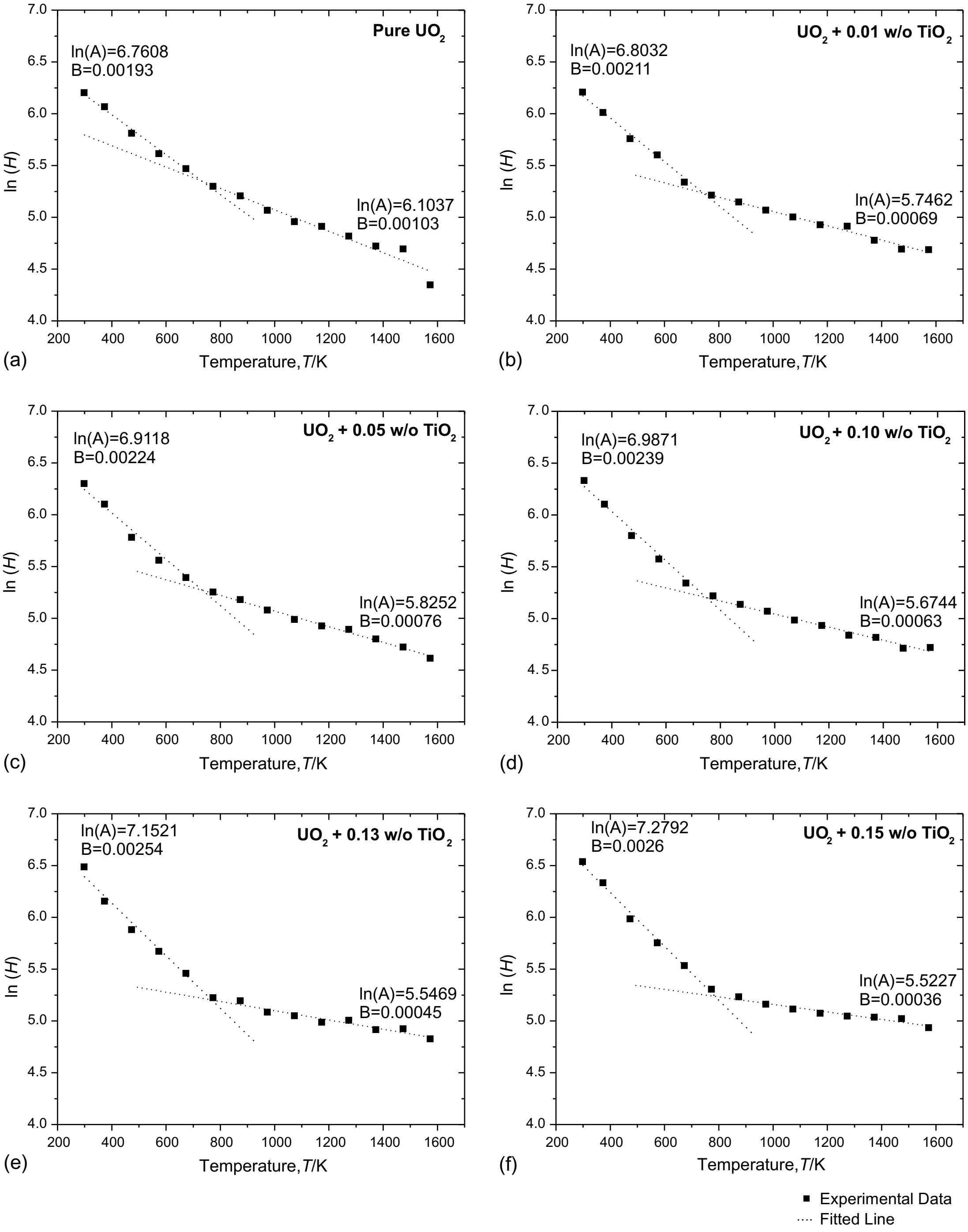


Fig. 5. Linear fit of ln$H$ vs. T. plot indicating two sets values for A and B depending on the temperature range as depicted in the figures.

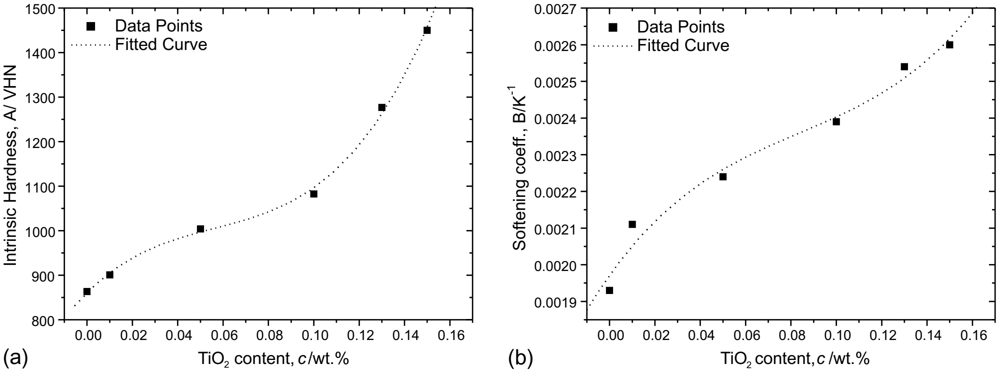


Fig. 6. (a) Plot showing intrinsic hardness (A) as a function of TiO_2 content and (b) softening coefficient (B) as a function of TiO_2 content.

impurities, grain size etc. The slope of $\ln H$ vs. T gives the softening coefficient (B). Since the deformation mechanism, as stated earlier, is different in the lower temperature range than that at higher temperature range; a distinct change in slope (i.e. $\mathrm{d}(\ln H)/\mathrm{d}T$ or B) is expected between lower and higher temperature regimes. Fig. 5(a)–(f) show the plot of $\ln H$ vs. T for various TiO_2 content which conform reasonably well to the exponential relationship between hardness and temperature. It is observed that the change in slope (i.e. $\mathrm{d}(\ln H)/\mathrm{d}T$) or the transition occurs between 600 and 800 K; depending upon the TiO_2 content. This transition refers to change in deformation mechanism. Below 700 K, the rapid decrease in hardness with the increase of temperature could be attributed to the release of strain energy (due to titanium ion and other interstitials) by lattice dilation. Beyond 700 K the rate of decrease in hardness is less due to the pinning of dislocations by the interstitials and fine precipitates of eutectic phase; such mechanism ensures that the variation in hardness is insensitive to temperature at least up to 0.6 T_m [15]; resulting in lower value of $\mathrm{d}(\ln H)/\mathrm{d}T$ at high temperature regime. Fig. 6(a) and (b) show the variation in intrinsic hardness (A) and softening coefficient (B) as a function of TiO_2 content respectively. As stated earlier, both A and B, in any specific temperature zone, are dependent on grain size as well as composition (TiO_2 content), and since grain size itself is a function of composition, A and B could be expressed as a function of composition alone in the present investigation where all other sintering parameters contributing to grain size enhancement have been kept constant. A and B are found to hold a cubic relationship with TiO_2 content (c).

$$A = 861.1077 + 5064.1915c - 66\,750.3622c^2 + 396\,152.3478c^3, \tag{2}$$

$$B = 0.00197 + 0.00865c - 0.07204c^2 + 0.2867c^3. \tag{3}$$

Eqs. (2) and (3) are valid for TiO_2 content of $c \leqslant 0.15$ w/o at $T \leqslant 673$ K. As TiO_2 content goes up the misfit strain increases which gives rise to higher intrinsic hardness value whereas with the lattice dilation (i.e. increasing T) more strain energy is released that caused higher value of softening coefficients as TiO_2 content increases.

4. Conclusions

- Grain size increases with increase in TiO_2 content. The increase is 9.5 μm to 94 μm corresponding to TiO_2 content 0.01 to 0.15 w/o respectively.
- Hardness increases with increase in TiO_2 content.
- Effect of grain size on hot hardness can be classified into three categories depending upon the temperature. At $T < 773$ K (500 °C), hardness decreases with increase in grain size, attains a minima and increases again at a faster rate with further increase in grain size. At higher temperature the hardness decrease very slowly with increasing G, attains a minima (not much prominent) and then increases with increasing G.
- For each sample, hardness decreases with increase in temperature and there is a change in hardness profile at an intermediate temperature due to change in deformation mechanism. For each temperature, there is one set of A and B. depicting the intrinsic hardness and the softening coefficient.
- The intrinsic hardness and softening coefficient summarized for the experimental samples as a function of TiO_2 content below 673 K.

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