

In-situ XRD Investigations Of Two Step R-phase Transformations In Aged NiTi Shape Memory Alloys

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Abstract: The characteristics of R-phase transformations in aged Ti-49.83 at% Ni (Nitinol) shape memory alloys at 300°C were explained with the help of Differential scanning Calorimeter (DSC) and In-situ X-ray Diffraction (In-situ XRD) studies. The solutionized and short duration aged samples (0 h and 48hrs) did not alter the B2-B19' transformation path and medium aged samples (72 and 96 hrs) exhibit single-step R-phase with B2-R-B19' transformation path and pro-longed aged sample (125 hrs) evolves two-step R-phase transformations with B19'↔R1↔R2↔B2. The carefully crafted in-situ XRD studies showed emerging of B2 (110) phase from merging of R (011) and R (-101) at 100°C and it is equal to the transformation temperature determined by the DSC experiments. The two-step R-phase transformation behavior is attributed to structural inhomogeneity of the matrix, both in terms of composition and of internal stress field, caused by the formation of Ni₄Ti₃ precipitates.

1. Introduction

It is widely known that thermoelastic martensites play an important role in the shape memory and pseudoelasticity in NiTi shape memory alloys [1,2]. The main disadvantage of these alloys is high sensitivity towards their transformation temperatures which makes them almost impractical in most of the vital practical application [3]. Hence, the lot of the ways are available to tune the transformation temperature sequences in a highly controlled manner for example: ageing treatment, thermo-mechanical treatment, etc., which makes much easier to design the shape memory alloys with narrow hysteresis losses will improve the performance of many practical systems [4,5]. The transformation sequences of the ageing characteristics of the NiTi shape memory alloys are widely studied in the last few decades. The near equiatomic NiTi shape memory alloys exhibit three different phases, the B2 phase, which has a CsCl structure, the B19' phase, which is monoclinic, and the R-phase (R), which is Rhombohedral [3,6-8]. The B2 phase is often referred to as the austenite (A) whereas the B19' phase is referred to as the Martensite (M). All three transformations involve lattice distortions and are martensitic in nature. Consequently, the transformations are sensitive to variations in metallurgical and mechanical conditions as well as chemical composition. Therefore, under different pretreatment and testing conditions, with the interplay of transformation hysteresis, various combinations of these transformations have been observed [2,9-11]. In addition to the usual transformation sequences in an aged sample shows some intermediate R-phase transformations also [12,13]. This paper attempts to clarify some of the correspondence of emerging of the B2 (110) phase from the merging of R-phases R(011) and R(-101) and the transformation temperature determined from in-situ XRD and DSC studies.

2. Experimental details

Ti-49.83% Ni (Nitinol) Shape memory alloy rod (12 mm) was granted from US Navy. The rod was subjected to the hot rolling at 800°C with 30% reduction in each pass brought down the thickness of 1 mm. It was followed by cold rolling (20% reduction in pass) with intermediate annealing at 450°C for 10 minutes to obtain thin sheet of 0.5 mm in thickness. Thereafter, the samples were cut in to the dimensions of 15×5×0.5 mm. The cut specimens are solution treated at 850°C for 1 hour and quenched in to the water to obtain room temperature. Then, the samples were subjected to the ageing treatment, aged at 300°C for different time intervals i.e., 0 hours (as-quenched), 48 h, 72 h, 96 and 125 hours.

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The transformation behavior and characteristics of the transformation temperatures were determined using a DSC cell Perkin Elmer (Pyris Diamond) with the specimen weight between 15 mg up to 25 mg. The nitrogen gas flow 400 ml/min was maintained to make inert atmosphere during the course of the experiment. In DSC tests, specimen was heated up to 180°C and held 5 minutes to obtain thermal equilibrium, followed by cooling down to room temperature with heating and cooling rate of 10°C/ minute.

Phase analysis and courses of martensite (B19' and R phases) and austenite (B2) phases were investigated at various temperatures by In-situ X-ray diffractometry using Bruker-D8 diffractometer equipped with a hot chamber. Diffraction patterns in Cu-K α radiation were recorded during cooling and heating rates of 1°C/min within the temperature range from 25 to 150°C. The phase analysis of the XRD peak profile was done by comparison with the standard JCPDS index.

3. Experimental results

3.1 DSC studies

Fig.1 shows the DSC measurements of the transformation behavior of a solution treated and water quenched specimen at 850°C for 1 hour. It is seen that the solution treated specimen exhibited single step transformations both on heating as well as during cooling with a thermal hysteresis of 37 K and it corresponds to the well established B2 \leftrightarrow B19' transformations [13]. However, the sample aged for 48 hours also shows the same transformation behavior with increase in thermal hysteresis of 41 K as compared to the solution treated specimen shown in DSC plot in Fig. 2. In contrast to the sample solutionized and aged for 48 hours, the material aged for 72 hours shows two-stage transformation on heating with the total thermal hysteresis of 60 K on heating cycle of the DSC plot, which is shown in Fig.3. The first stage of the transformation corresponds to the formation of the R-phase from the B19' monoclinic Martensite phase and the second step corresponds to the B2 Austenitic phase transformation from the R-phase. The nucleation of the R-phase martensite incorporates with the formation of the Ni₄Ti₃ precipitates from the supersaturated B2 (cubic) austenitic matrix. The deepening of the R-phase peak was inferred in the sample aged for 96 hours shown in Fig.4. The two-step R-phase transformation occurred in the material aged for 125 hours shown in Fig.5.

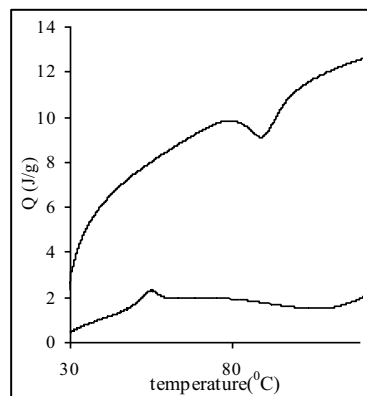


Fig. 1 DSC plot of the NiTi alloy solutionized at 800°C for 1 hr followed by water quenching to room temperature

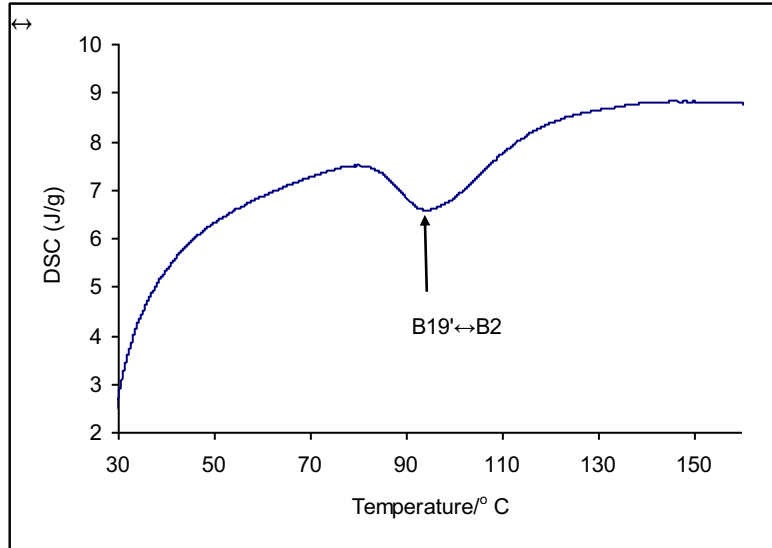


Fig. 2. DSC study of NiTi alloy aged at 300°C for 48 hrs

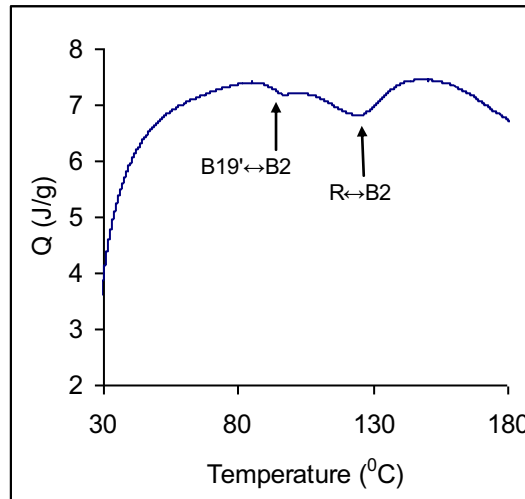


Fig. 3 DSC study of NiTi alloy aged at 300°C for 72 hrs.

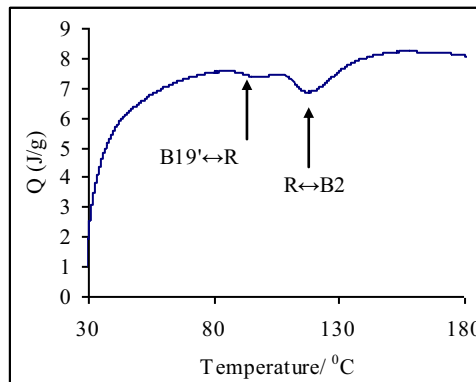


Fig. 4 DSC study of NiTi alloy aged at 300°C for 96 hrs

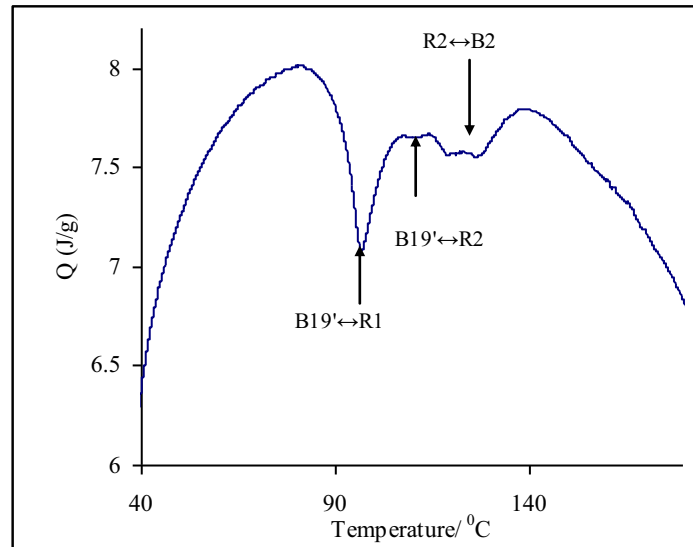


Fig. 5 DSC plot of the NiTi shape memory alloy aged at 300°C for 125 h

3.2 In-situ XRD studies

The room temperature XRD pattern of the aged NiTi specimen aged at 300°C for 125 h is shown in Fig. 6. The XRD peak profile was indexed with the standard JCPDS data and the corresponding analysis of phase, planes and 2θ values as follows: 2θ at 41.4° M(111), 42.31° R(011), 42.45° (101), and 43.85° M(020). Henceforth, the identified phases correspond to the mixed microstructure of the B19' and R-phases. Fig.7 shows an XRD experiment performed at 100°C of the NiTi specimen aged at 300°C for 125 h. There was distinguishable difference in the X-ray diffraction peak positions compared with those observed at room temperature. It shows vanishing of the closely located peak and vertebrate difference in the shoulder peak position at 100°C rather than those appeared at room temperature. The analysis of the peak profile showed the existence of R(011) and R(-101) phases along with B2(110) phase and it was confirmed that no distinguished peak avail for the B19' phase. There is a single dominating peak found at 150°C was shown in Fig. 8 corresponds to the high temperature phase of B2 along with the (110) plane. The carefully crafted in-situ X-ray diffraction studies conducted from 25°C to 150°C was shown in Fig.9 Even though, the interpretation of temperature region in this figure was difficult, it is wisely understood that increasing temperature leads to the emerging of the B2 phase from merging of the R-phases.

4 Discussion

4.1. Evolution of the R-phase transformations with respect to the ageing time

It is evident from the experimental results presented above that ageing under certain conditions may induce three-step transformations behavior in Ni-45.08 wt% Ti SMAs. The results presented in Fig. 1-5 demonstrated that the first R-phase peak transformations occurred in the prolonged aged durations, aged for 72, 96, and 125 hours. But, the second R-phase transformations appeared in aged only for 125 hours sample (B19'→R1→R2→B2). And, the second R-phase transformation is emerged along with the B2-phase, called as R2. Thermal hysteresis observed in this R2 (Rf-Rs) is 10 K (higher temperature R-phase) very much lower than the early-formed low temperature R-phase transformations in aged for 72 and 96 hrs, which is 26K. The total endothermic energy (ΔH_T) of this absorbed in this aged sample is 6.41 J/g, which is equal to the sum of the ΔH_T ($\Delta H_T = \Delta H_{R1} + \Delta H_{R2} + \Delta H_{B2}$). Thermal hysteresis observed in the B2 cubic phase transformation is 14 K (in aged for 125 hrs NiTi), lesser than earlier aged samples, aged for 0 h (as-quenched), 48 h, 72h, and 96 hours, which shows that less lattice distortions are required to nucleation of the formations of the R2→B2 transformations, as compared to the higher lattice distortions observed in

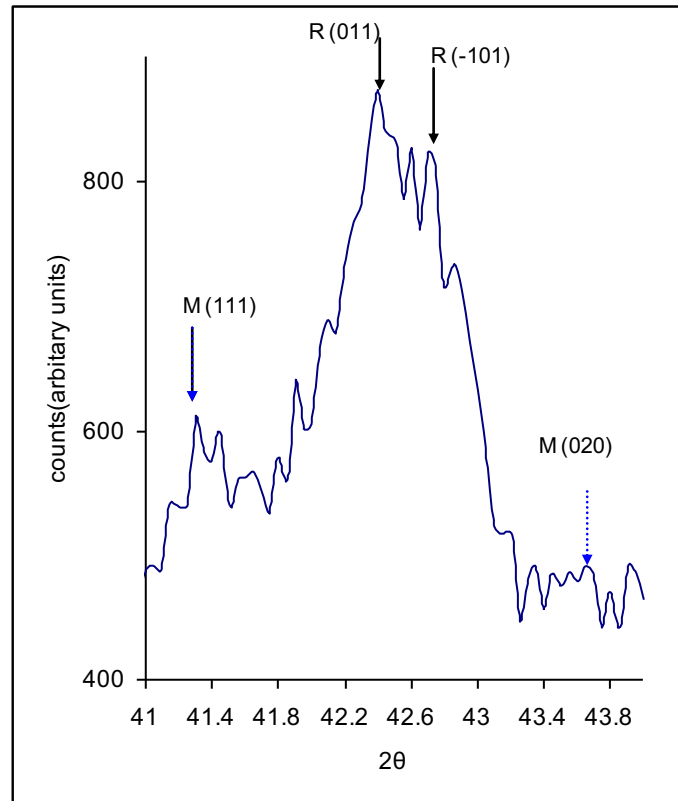


Fig. 6 XRD peak profile at normal operating temperature at 25°C, shows mixed peaks of B19', R1 and R2.

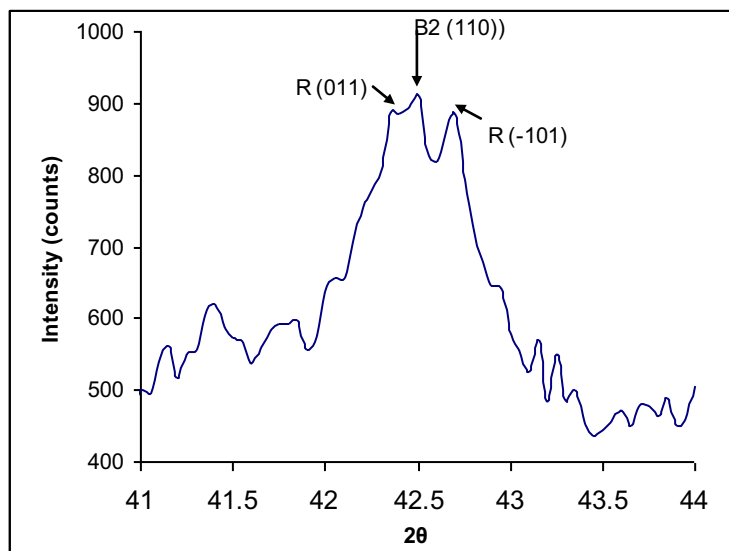


Fig. 7 In-situ XRD peak profile at 100°C exhibits B2, R1 and R2 peaks.

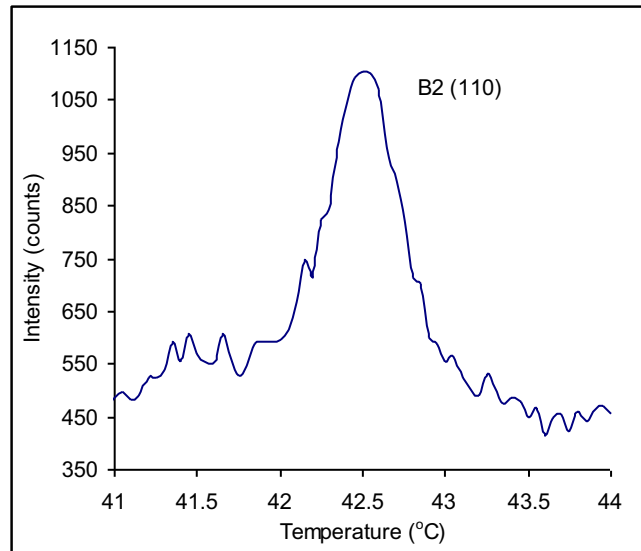


Fig. 8 In-situ XRD Peak profile at 120°C shows only B2 phase without intervene of R1 and R2 phases

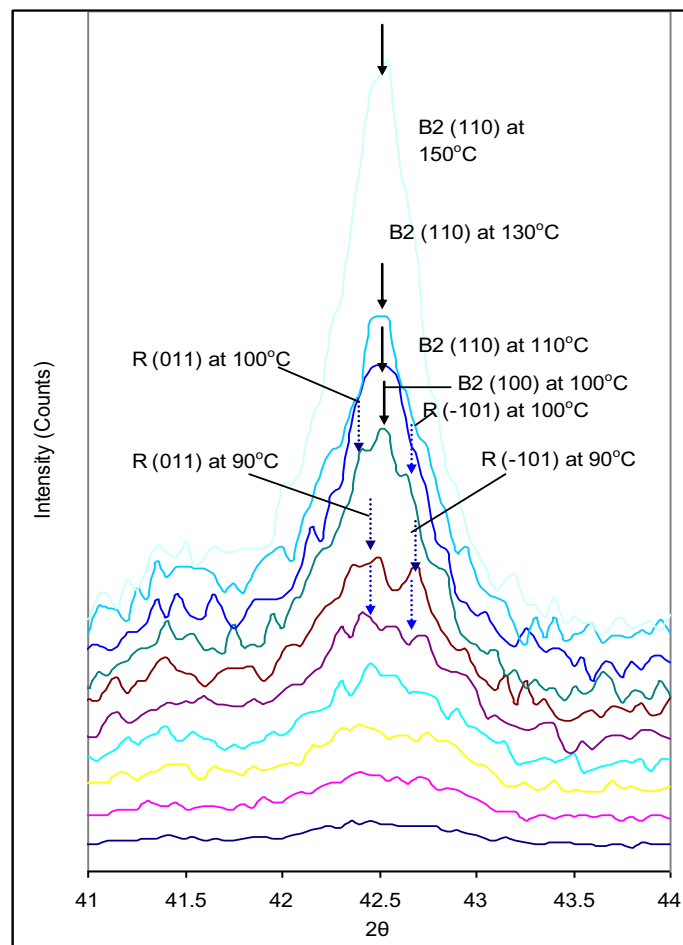


Fig.9 In-situ XRD peak profile at different temperatures shows emerging of B2 (110) phase from merging of R(011) and R(-101) phase.

other aged samples ($B19' \rightarrow R$). The reason for the formations of the R2 phase transformations in peak aged sample is due to the formations of the scattering of the Ni_4Ti_3 precipitates; it means heterogeneous Ni_4Ti_3 precipitates, which is not observed in single step R-phase transformations, inside the grain boundary as well as along the grain boundary [3]. So, the total transformation sequences in the sample aged for 125 hours is as follows: $B19' \rightarrow R1 \rightarrow R2 \rightarrow B2$, however, in the case of the samples aged for 72 and 96 hours the sequence is only $B19' \rightarrow R \rightarrow B2$. Three step transformations were observed in the samples aged for 125 hours in NiTi SMAs, 2-step transformations were observed in samples aged for 72, and 96 hours, and single step transformations was observed in samples aged for 0 h (solutionized) and aged for 48 hours. So, we propose the new transformation sequence of the 0-1-2 model for the explanation of the R-phase transformations [15]. The explanation for the above sequences on heating cycle from $B19'$ to B2 are as follows: (0) for low ageing period $B19' \leftrightarrow B2$ (0 and 48 hrs), (1) for medium ageing period $B19' \leftrightarrow R \leftrightarrow B2$ (72 and 96 hrs) and (2) for pro-longed aged period the phase sequence was $B19' \leftrightarrow R1 \leftrightarrow R2 \leftrightarrow B2$ (125hrs). Reportedly, the R2 phase transformations having very low thermal hysteresis and required very low endothermic energy, as compared to the ordinary R-phase transformations, so, it may be useful in the design of the low thermal hysteresis devices [3]. Surprisingly, the transformation temperature reported in our studies is much higher than the transformation temperature reported elsewhere [3,6,13,15]. This peculiar high transformation characteristic of this NiTi samples will be much useful to design devices for room temperature and elevated temperature applications. Unfortunately, we could not be able to measure the cooling sequences of these transformations; it would give us some important information. The following points can be summarized from the above discussions regarding two-stage R-phase transformations:

1. Aged Ni-45.08 wt% Ti shape memory alloys at 300°C for 125 h were effective in inducing a two-stage R-phase transformation behavior involving two separate stages of the $B19' \rightarrow R$ transformation followed by a one-step $R \rightarrow B2$ transformation. During ageing, the volume fraction of the first $B2 \rightarrow R$ transformation increased at the expense of the second $R1 \rightarrow R2$ transformation [3]. Accompanying the appearance of the $B2 \rightarrow R$ transformations coherent Ni_4Ti_3 precipitates were formed in the matrix. The two-stage transformation behavior is attributed to the structural inhomogeneity of the matrix, both in terms of composition and of internal stress field, caused by the formation of these precipitates.
2. The first $B19' \rightarrow R$ transformation on heating is identified as the transformation in regions within the vicinity of Ni_4Ti_3 precipitates. The second $R \rightarrow R2$ transformation at a higher temperature is identified as the transformation in regions away from the precipitates. The $B19' \rightarrow R$ transformation following the R2-phase transformations is identified as the transformation of the R-phase formed in the second $B2 \rightarrow R$ transformation, i.e., the R-phase formed in the matrix away from the precipitates. The transformation of the R-phase formed in the vicinity of precipitates, we believed it might be a lower temperature [3].
3. With the introduction of the R-phase transformation in the transformation sequence by ageing, the martensitic transformation changed from $B19' \rightarrow R \rightarrow R2 \rightarrow B2$. These are attributed to two-contributions: (i) change of transformation sequence and (ii) mechanical resistance of the matrix towards internal shape changes. The variation of mechanical resistance of the matrix is related to the evolution of morphology of Ni_4Ti_3 precipitates.
4. $T^{B19' \rightarrow R}$ is attributed mainly to the depletion of Ni-content in the matrix and in the vicinity of Ni_4Ti_3 precipitates and the effects of internal stresses created by the formation of the precipitates. But the sudden decrease? in the R_s temperature may be due to the formation of the heterogeneous Ni_4Ti_3 precipitates associated with the formation of the R2-phase.

The occurrences of the two separate transformation peaks ($B19' \leftrightarrow R1$ and $R1 \leftrightarrow R2$) signifies two different free energy states of the R-phase relative to the $B19'$ phase transformations on the heating cycle of the DSC plot. It is certain that the two-step R-phase transformation behavior is associated with the formations of the precipitates. The formation of fine, coherent Ni_4Ti_3 precipitates has two consequences that may affect the transformation behavior of the matrix: (1) change in matrix compositions and (2) creation of local stress fields. In the context of ageing, it is suggested that R is the phase formed around precipitates, i.e., formed in “affected zones”, whereas R2 is the R-phase formed regions away from the precipitates. i.e., in the “unaffected” matrix [3]. This identification was suggested from the following experimental observations:

1. R2 is the phase appeared in between $T^{R \leftrightarrow B2}$ of the aged for 125 hours sample, and $T^{R2 \leftrightarrow B2}$ is compatible to that expected for the R2 phase transformations.
2. R-phase transformations appeared initially well above the original $B19' \leftrightarrow B2$ cubic phase transformations in aged for 72,96 and 125 hours [13, 15].
3. During ageing $T^{B19' \leftrightarrow R}$ increased well more, as a result of continuous change in matrix compositions caused by precipitations, than did $T^{B19' \leftrightarrow B2}$, because that conditions (Compositions) favors for the R-phase transformations in the “affected” zones are excepted to very less than those in the matrix [3].

4.2 Discussion of In-Situ XRD studies

The main objective of this present paper to provide the correlation between the phases and transformation temperatures identified from DSC and XRD studies. The B19', R1, R2 and B2 phases evolved in NiTi shape memory alloys aged at 300°C for 125 h. This sample was chosen to carry out in-situ XRD studies using Bruker-D08 XRD instruments. The temperature of the specimen in the range from 25°C to 150°C was controlled with the help of a filament heater situated beneath the sample holder.

Fig.9 shows the XRD spectra of the NiTi aged sample at 300°C for 125 h at room temperature. It can be easily seen that three undistinguished closely located peaks are found and indexed as 2θ at 41.4° M(111), 2θ at 42.31° R(011), 2θ at 42.45°, 2θ at R(-101), and 2θ at 43.85° M(020). Basically, the room temperature microstructure is a mixture of the B19' and R-phases. It is happening mainly due to the rhombohedral distortions of the R-phase into the parent lattice of B19' matrix. There are complicated but clearly distinguishable closely located two peaks that correspond to the R-phase; there was only slight elevation differences in their peak positions at their shoulder elevation level {R (011) located in higher elevation of the shoulder as compared to the R (-101)} and it could be firmly identified as first peak R (011) at $d=2.13 \text{ \AA}$ and second peak R (-101) at $d=2.121 \text{ \AA}$. This specimen was heated to the high temperature in diffraction chamber with the help of the filament heater located beneath to the specimen holder and the heating rate was 1°C/min and the In-situ XRD was performed at 150°C. It is clearly seen that there could be only one distinguished peak avail at $2\theta=42.505^\circ$ corresponds to the B2 (110) phase. There was no trace of ups and downs of other peaks. Thereafter, the specimens temperature was decreased systematically with the cooling rate of 1°C/min with close control to 130°C, however, no change in the peak position and it is quite clear that B2 phase was quite stable without intervening of the other phases and intensity of the peak (I/I_0) was 850 counts. However, XRD spectra of the B2 phase at 110°C was not so sharp as compared to the XRD spectrum at 130°C, it is mainly due to the decreasing intensity of the (I/I_0) along with the peak broadening effect proves that B2 phase was not quite stable further lower temperature. Furthermore, the temperature of the sample was cooled down to 100°C and in-situ XRD peak profile shows there is no longer existence of the single dominating peak found in their earlier temperature experiments at 110 °C rather it is the mixture of the B2, R1 and R2 phases. The same situation was observed in-situ XRD performed at 90°C also. However, when the temperature of the diffraction studies further down below to 90°C governs only R-phase and B2 phase is not existence in this vicinity of temperature range. While doing this interpretations with the standard index, it is identified that presence of the R-phase (011) plane at $d=2.153 \text{ \AA}$ and R(-101) peak at $d=2.11 \text{ \AA}$ and the corresponding peak broadening also visible without any sharp single peak [3]. It is clear that the formation of the R-phase involves fluctuations in their local composition and as a result dilatation in their d-spacing values inscribed formation of the two-phase R-phase transformations. As temperature of the specimen decreased still further down, the intensity of the R-phase peak is increased promptly, proves that R-phase is highly stable at temperature below 90°C and increasing intensity of the B2 phase with increasing temperature states that stability of the B2 phase increases with increasing temperature above 90°C.

The R-phase peaks R(101) and R(011) are corresponds to the $2\theta=42.35^\circ$ and 42.5° are shows lucrative distinguish in their peak intensity variations with respective to the temperature are shown in Fig.10.

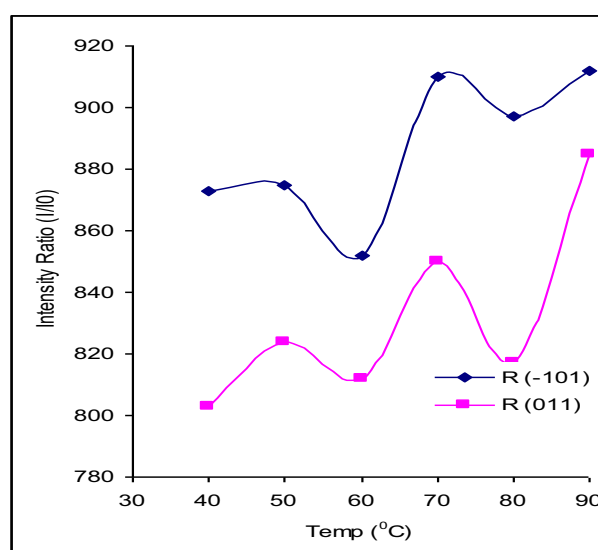


Fig. 10 shows intensity ratio comparisons between R(101) and R(011) confirms R-phase reaches maximum temperature at 90°C.

The rhombohedral distortions of the R (-101) and R (011) was not following any systematic trend was explicit from the intensity ratio respect to the temperature profile [16]. However, intensity of the R-phase decreases with increasing temperature of this study, whereas, J. I. Kim et al., [3], studied for intensity count profile for R-phase at (101) plane in NiTi aged at 200⁰C was compared with this present experimental studies. The intensity of R (-101) peak varied abruptly with increasing temperature of the diffraction experiments as compared to the R (011), is due to the formation of this phase depends upon energy required for nucleation of the Ni₄Ti₃ precipitates. It signifies two different free energy states (1-change in matrix compositions and 2-creation of local stress fields)of the R-phase relative to the B19' phase. The intensity of the R (-101) was increased promptly from 50⁰C to 70⁰C (neglecting at 60⁰C) explains distortions of the rhombohedral phase in the B2 matrix increases drastically, however, it has to over come the finite energy barrier between the Ni₄Ti₃ precipitates and the transformation strain which accompanied volume changes observed from the B19' to R1 phases. In the case of interpretation of the rhombohedral distortion of R phase in (011) plane was not showing any abnormality in their intensity count profile suggests that growing of Ni₄Ti₃ precipitates was not prompted and at the same case it is not sluggish; it follow homogeneous and regular growth behavior from the distortions of B19' monoclinic phase to accommodate the volumetric shape strain produced from B19' to R phase on heating. The large changes in the intensity counts in the R (-101) dictates large differences in the energy barrier level between B19' to R2 phase on heating, which hinders nucleation of the Ni₄Ti₃ precipitates and of-course, changes in the formations of the size of the precipitates also. Henceforth, it is certain that the two-step R-phase transformation behavior is associated with the formations of the precipitates. R(011) phase also shows the same behavior except that the steep gradient was not noticed in the R(-101) peak. It flaws clearly, definite change in the local-heterogeneous compositional fluctuation increases with increasing ageing time was observed with their shifting of peak position. The change in heterogeneous composition fluctuations arises mainly due to the formation of the Ni₄Ti₃ precipitates alters local stress fields in and around the precipitates. Such composition in homogeneous is a result of the kinetics of precipitation process out of a supersaturated solid solution. The composition inhomogeneity between Ni₄Ti₃ particles would create one B2-R transformation and two R-B19' transformation, the latter corresponding to the transformation at low Ni region (near Ni₄Ti₃) and high Ni region (away from Ni₄Ti₃) respectively. [13]

4.3 Comparison of DSC and In-situ XRD studies

There is a certain undisputed relationship between the transition temperature determined from in-situ XRD and DSC plot for NiTi sample aged at 300⁰C for 125 h. However, it is the tedious work to determine the transition temperature using XRD unless otherwise if it is known the probable transition temperature range. Henceforth, we use DSC plot to determine the A_s temperature and it was found that it falls at 90⁰C and of-course by carefully crafted in-situ X-ray diffraction studies also shows roughly the same temperature region; but we have not conducted in-situ XRD studies at 85 to 89⁰C and if you could do so it may be end up with some controversial discussions about the determination of the B2-phase transformation temperature from the R-phase. However, it could roughly fall on this same temperature region. Hence, the transformation temperature determined from the in-situ XRD studies is proven more or less equal to the predicted temperature from the DSC studies.

5. Conclusions

The following important conclusions were drawn from the above analysis listed as follows:

1. The effects of ageing induced changes in the phase transformation sequences of NiTi shape memory alloys at 300⁰C for different time intervals were explained with the DSC and XRD studies and we propose new phase transformation sequences are as follows: 0-1-2. The explanation for the above sequences on heating cycle from B19' to B2 are as follows: (0) for low ageing period B19'↔B2 (0 and 48 hrs), (1) for medium ageing period B19'↔R↔B2 (72 and 96 hrs) and (2) for pro-long aged period B19'↔R1↔R2↔B2 (125hrs)
2. R-phase transformations appeared initially well above the original B19'↔B2 cubic phase transformations in aged for 72,96 and 125 hours.
3. Carefully crafted In-situ XRD studies in NiTi aged at 300⁰C for 125 h sample was shown emerging of the B2 phase at (110) plane from merging of the two-R phases at R(011) and R (-101) at 100⁰C and it is more or less matching with the transformation temperature determined by the DSC studies also.
4. The large changes in the intensity counts in R (-101) dictates large differences in the energy barrier level between B19' to R2 phase on heating, which hinders nucleation of the Ni₄Ti₃ precipitates and of-course, changes in the formations of the size of the precipitates also. Henceforth, it is certain that the two-step R-phase transformation behavior is associated with the formations of the Ni₄Ti₃precipitates.

5. Similarly, R(011) phase also shows the same behavior except that the steep gradient was not noticed in the R(-101) peak. It flaws clearly, definite change in the local-heterogeneous compositional fluctuation increases with increasing ageing time was observed with their shifting of peak position. The change in heterogeneous composition fluctuations arises mainly due to the formation of the Ni₄Ti₃ precipitates alters local stress fields in and around the precipitates.

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