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B19 orthorhombic martensitic Transformations in Aged TiNiCu Shape Memory Alloys

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Abstract: This paper gives details about the B19-rhombohedral martensitic transformations in $TiNi_{44.5}Cu_{5.5}$ Shape Memory Alloys (SMA) aged at 150^0C. The martensitic phase transformation sequences observed in this present study by using differential scanning calorimeter (DSC) as follows: As-solutionized and aged for 4 hrs samples exhibits B19↔B2; Aged for 24 h, 48h and 72 h sample exhibits B19↔B19'↔B2 and pro-longed aged sample for 96 hrs exhibits B19'↔B2 transformations. The strong diffraction peak can be identified as the (020)B19 in TiNiCu aged at 150ºC for 24 hrs. It is clear from X-ray diffraction phase analysis formation of equilibrium Ni_3Ti (S.G. $P6_3$/mmc (194), Hexagonal crystal structure) precipitates reaches maximum counts with (020) plane in aged for 48 h sample as compared to the aged for 24 h sample. The high DSC values (J/g) of the exothermic peak was recorded in aged for 48 hrs samples was concluded formations of the B19' martensites.

1. Introduction

The characteristics of near equiatomic NiTi binary Shape memory alloys SMAs will be affected by the addition of a third element like Cu, Fe and Pt [1-2]. An addition of third element can largely increase damping capacity [3]. For example, TiNiCu SMA with a small amount of Cu being substituted for Ni will result in a smaller transformation hysteresis, less Ms sensitivity to compositional variations, more constant Ms independent of cycling, prevention of Ti_3Ni_4 precipitation [4, 5] and larger damping capacity than those of NiTi binary SMAs. Furthermore, it has been confirmed that the parent phase of the alloy remains to be a single B2 phase and the shape memory effect still appears while up to 30at. %Cu is substituted for Ni in the binary NiTi SMAs. The alloys become brittle while more than 10at. %Cu is substituted for Ni in the NiTi SMAs [6,7]. The addition of 5 at% Cu in substitution of Ni to the NiTi binary alloy changes martensite transformation in two steps - from cubic B2 parent to orthorhombic B19 martensite and from orthorhombic B19 martensite to monoclinic B19' martensite [8]. TiNiCu alloy exhibits a very high damping peak. Aging effect was also found in ternary Ti–Ni–Cu alloys with Ti-poor compositions (less than 50 at.%) [9, 10] . In such a case, a new kind of precipitate Ti(Ni-Cu)2 with tetragonal $C11_b(MoSi_2)$-type structure was found. During the precipitation of such particles by aging treatment, it was found that martensitic transformation temperature increases to some extent.

In this paper, results on martensite ageing behavior incorporated with Ni_3Ti precipitates in a NiTiCu shape memory alloys at 150^oC are reported. The characteristics of the two-stage martensitic transformation B2-B19-B19' in aged samples were explained with the help of DSC and XRD studies. It was found that increases in the endothermic energy of the heating cycle of the DSC plot was due to the formation of equilibrium Ni_3Ti precipitates during ageing from the B19 martensites.

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2. Experimental

The investigated alloys were polycrystalline NiTiCu (NiTinol-Cu) SMA in the form of 12.5 mm rod granted from Naval-Air systems Command, Maryland, USA. After hot rolling followed cold rolling, the thickness of the sample was reduced to 0.5 mm. This sheet samples were solution treated at 800^0C for 1 hour and quenched in to water to retain B19-martensite phase. Then the samples were subjected to the ageing treatment at 150^0C for different periods 0 h (as-quenched), 4, 24, 48, 72 and 96 hours.

Transformation temperatures were determined using Differential Scanning Colorimeter (DSC), DSC-Perkins (Pyris Diamond), with controlled heating as well as cooling (10 K /min), in an Nitrogen gas atmosphere, flow rate of nitrogen gas equal to 400 ml / minute.

Crystal structure of the phases were determined using powder X-Ray diffractometer (XRD), Bruker-D8, temperature of the testing chamber 25^0C, target Cu-Kα, scan step mode 0.01^0, 2θ angle was 30-60^o. The dimensions of the samples were 10 X 5 X 0.5 mm (L X W X T).

3. Results

Fig. 1 shows the DSC study of the as-quenched (Solutionized) NiTiCu SMA. The single step transformations was observed both on heating and cooling, indicates well established B2↔B19 (Rhombohedral martensites) [7]. The aged for 4 hrs sample also shows same transformation behavior similar to the solutionized sample was shown in Fig. 2. However, aged for 24 hours sample consists of two-step transformations on heating and single step transformations on cooling was shown in Fig 3. Unfortunately, we did not measure the transformation temperature on cooling for this sample. The two separate transformations step on heating suggests that the first transformations step corresponds B19'↔B19 and second transformation step corresponding to the B19↔B2, however, the endothermic energy involved in these transformations were very low and we may expect this may be the origin of interference of the B19' with B19 phase. Further aged for 48 h sample shows deepening of the DSC peak area due to the high endothermic energy

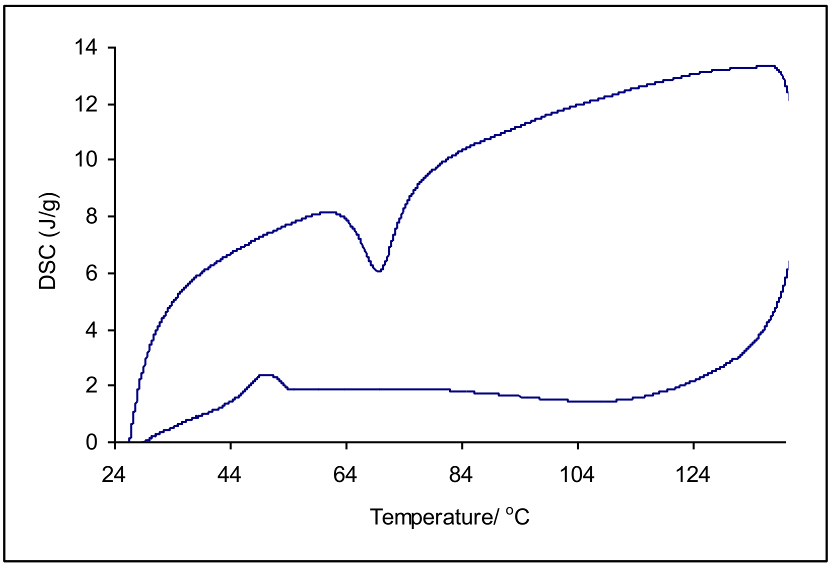

Fig. 1 DSC study of NiTiCu solutionized at 800^{o}C for 1 hr and quenched in to water to get room temperature.

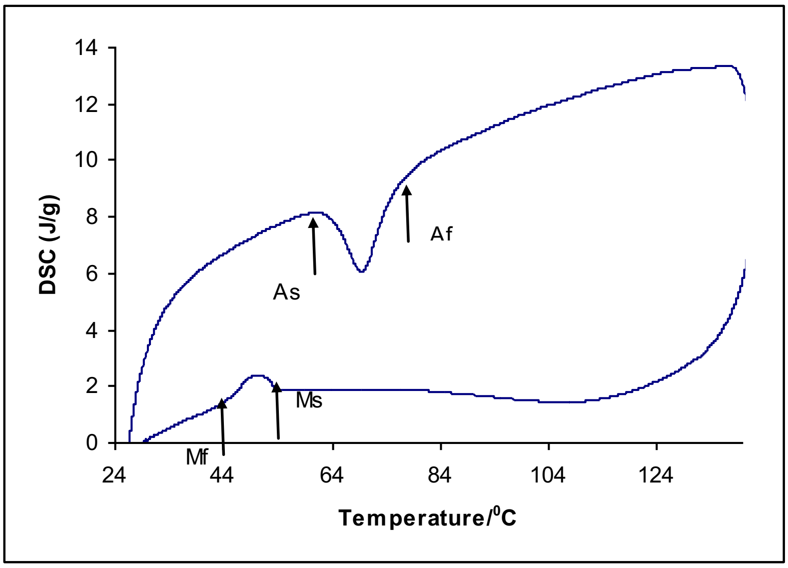

Fig. 2 DSC study of NiTiCu aged sample at 150°C for 4hrs

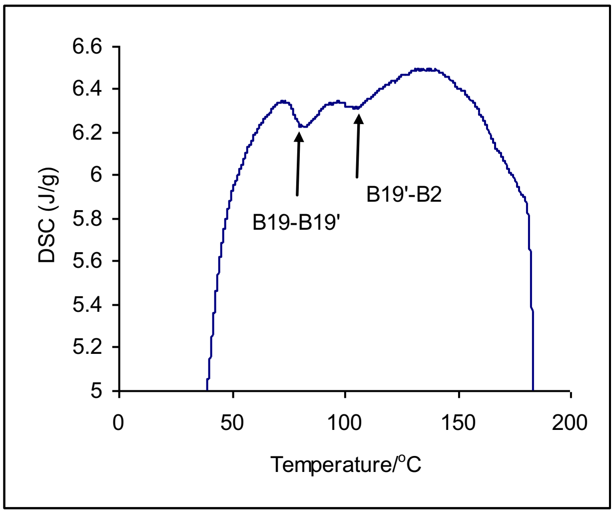

Fig. 3. DSC study of NiTiCu aged sample at 150°C for 24 hrs

incurred towards stabilization of the B19' phases took place at this intermediate ageing time was shown in Fig. 4. However, the stability of the B19 phases decreases in aged for 72 h sample was shown Fig. 5. The endothermic energy involved in this phase transformation was lower than aged for 48 h. Furthermore, increasing ageing time leads to the formations of the single step transformations than the two-step martensitic transformations observed in earlier aged samples. Fig.6 indicates single step transformations on heating cycle in aged for 96 hrs sample. The DSC values (J/g) increases as compared to the aged for 72 hrs samples. Only B19' martensites were observed in this sample rather than the B19 martensite [11] explained in discussions section Fig. 12 of this present paper.

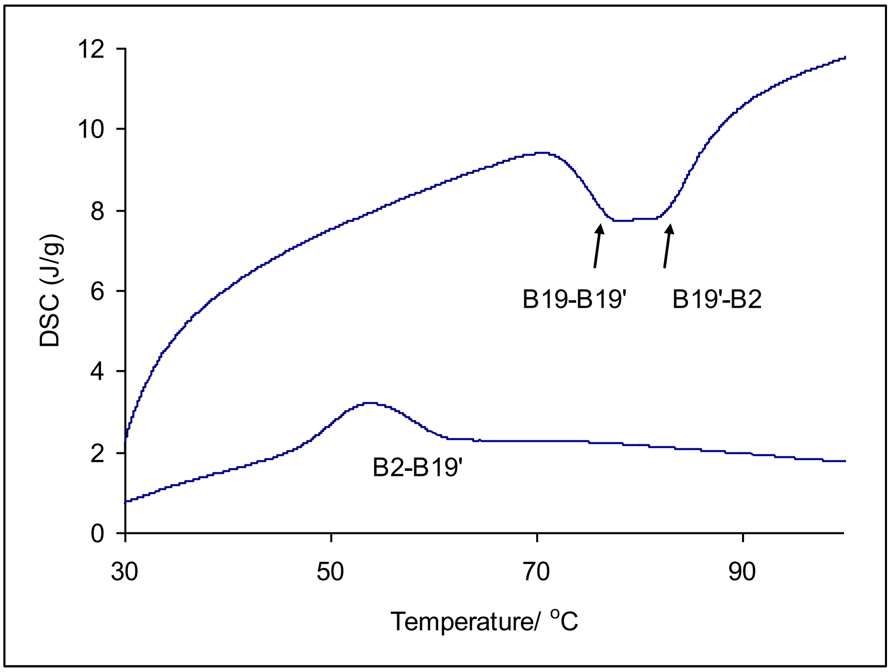

Fig. 4. DSC study of NiTiCu aged sample 150°C for 48 hrs

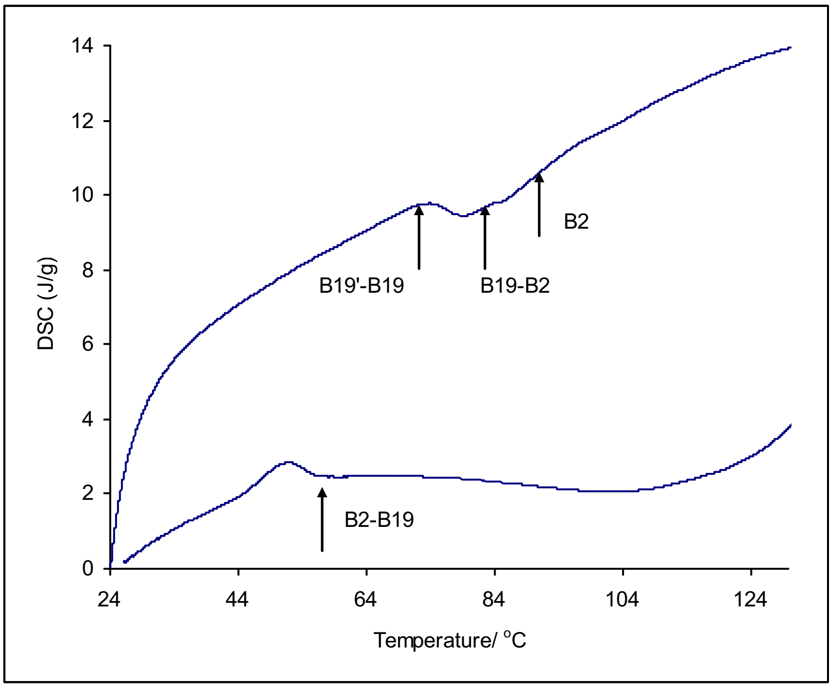

Fig. 5 DSC study of NiTiCu aged sample at 150°C for 72 hrs

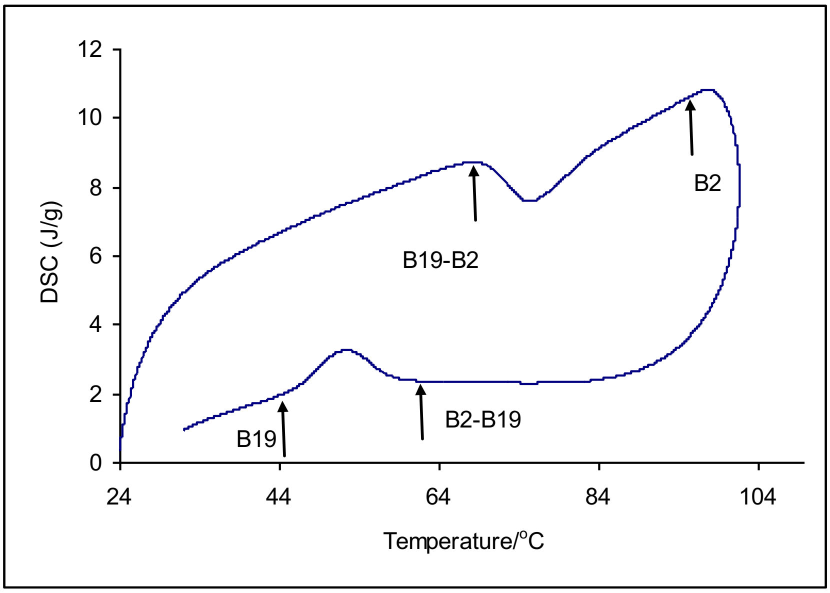

Fig. 6. DSC study of NiTiCu aged sample at 150°C for 96 hrs

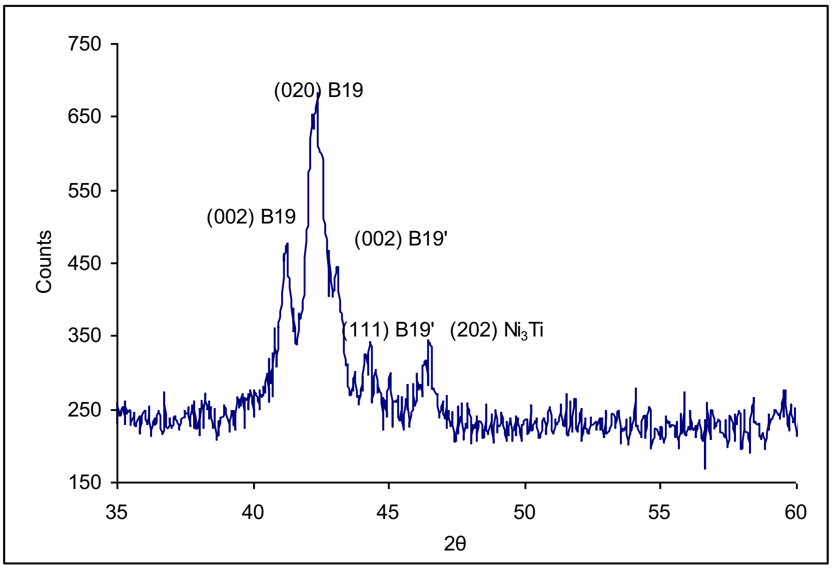

Fig. 7. XRD plot of NiTiCu sample aged at 150°C for 24 hrs exhibiting B19,B19' and Ni_3Ti precipitates

Fig. 7 indicates XRD phase analysis of the aged at 150ºC for 24 hr. The strong diffraction peaks were identified at 42.28º (2θ) corresponds to the B19 orthorhombic martensites with (020) plane [12]. The weak diffraction peaks were indexed as follows: B19- orthorhombic martensites corresponds to the planes of (002) at 41.21º (2θ) and B19'- monoclinic martensites with plane of (002) at 43.07º (2θ) and (111) at 44.25º (2θ), Ni_3Ti (S.G. $P6_3/mmc$ (194), Hexagonal crystal structure) precipitates corresponding to the plane of (202) at 46.67º. Fig.8 indicates XRD phase analysis of NiTiCu aged for 48 h sample. The first-strong diffraction peak corresponds to the Ni_3Ti precipitates with (202) plane, whereas, aged for 24 h sample was shown much lower intensity ratio (I/I_o) nearly equals to 20% and the second strong diffraction peak respect the formation of B19' martensites with (111) plane. This clearly emphasizes formations of Ni_3Ti precipitates along with B19' martensites play a major role in the deepening of the endothermic peak with high DSC values was 12.9 J/g in heating cycle of the DSC plot. This high endothermic energy values are summation of $\Delta H_{B19\text{-}B19'}$ and $\Delta H_{B19'\text{-}B2}$. The weak diffraction peaks are as follows: B19- orthorhombic martensites corresponds to the planes of (002) at 41.09º (2θ) and B19'- monoclinic martensites with plane of (002) at 43.17º (2θ) and (111) at 44.25º (2θ).

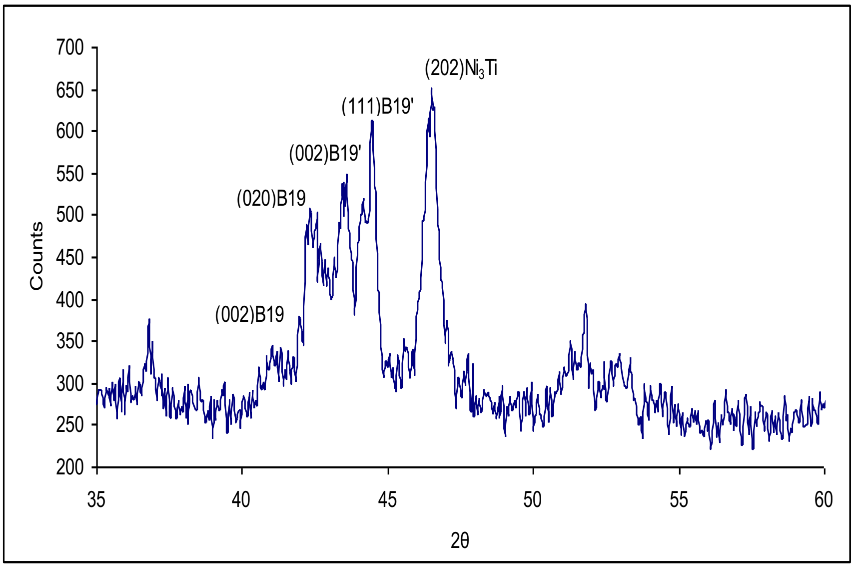

Fig. 8. XRD plot of NiTiCu sample aged at 150°C for 48 hrs exhibiting B19, B19'and equilibrium Ni_3Ti precipitates.

4. Discussion

Fig. 9 indicates the relationship between temperature differences in A_f-A_s as function of ageing time extracted from DSC studies. It is clear from this figure that decreasing ΔT values represents for the formations of equilibrium Ni_3Ti precipitates (Ref-XRD plot of Fig. 7 & Fig. 8) from B19 orthorhombic martensites. In aged for 48 h sample ΔT values further come down due to Ni_3Ti precipitates and B19' monoclinic martensites, because, the intensity ratio (I/Io) of Ni_3Ti observed in 48 h aged sample was 100% as compared to the I/Io observed in the 24 hr sample was 20%. However, furthermore ageing beyond this temperature range will no longer be the role of B19 orthorhombic martensites instead of B19' monoclinic

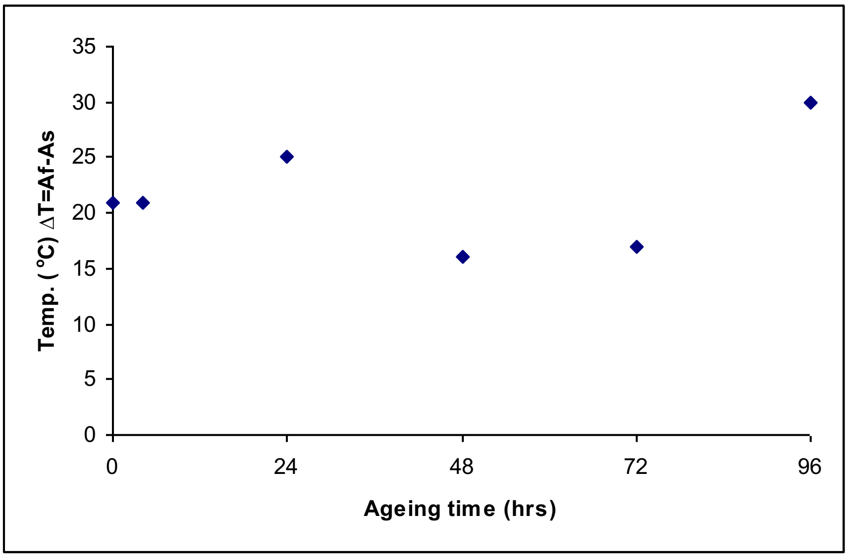

Fig.9 . The temperature differences between the A_f-A_s as a function of ageing time (hrs)

martensites plays crucial role to define the shape memory characteristics. This can be visualize from the increasing ΔT values beyond 48 h. Similarly, the highest endothermic energy was observed in aged for 48 h sample as compared to the prolonged aged for 96 h indicated in Fig.10. The lowest DSC values was observed in aged for 24 h sample may be nucleation of the equilibrium Ni_3Ti precipitates form B19 martensites identified from XRD profile. Therefore, the endothermic energy of this phase transformations was very low value about 0.4 J/g. As the ageing time increasing beyond 48 h will lead to the reduction in DSC values for 72 h due to the formations of the two-step transformation and further aged for 96 h exhibits single-step transformation causes increases in the DSC values as similar to the solutionized sample. Full Wave at Half Maximum values calculated from XRD plot of NiTiCu aged at 150°C for 24 and 48 hrs was shown in Table-1. It was found that FWHM (2θ) values for equilibrium Ni_3Ti precipitates are decreased from 0.59° in the case of aged for 24 hrs as compared to the 0.246° in the case of aged for 48 hrs and I/Io values are increasingly promptly from 19% to 100% respectively. Hence, it is clear that aged at 48 hr sample shows high I/Io values 100% as compared to the aged for 24 hrs. It implies stabilization of equilibrium Ni_3Ti precipitates were occurred in aged for 48 hr sample and it will lead to the increase in endothermic energy observed in heating cycle of DSC studies [9].

Table-1 FWHM (2 θ) values calculated from XRD plot of NiTiCu aged at 150°C samples

Sample	Peak	d (A°)	I/Io (%)	FWHM (2θ)
Aged for 24 hr	(002)B19	2.1885	54	0.295°
	(020)B19	2.1338	100	0.59°
	(202) Ni_3Ti	1.9509	19	0.59°
Aged for 48 hr	(002) B19	2.13	50	0.394°
	(002) B19’	2.07	64	0.295°
	(111) B19’	2.03	90	0.197°
	(202) Ni_3Ti	1.94	100	0.246°

Fig. 11 shows the exothermic energy (both B19 and B19’) evolved on reverse transformation on cooling varying with respect to the ageing time. The highest exothermic energy liberated aged at 48 h sample indicates heavy distortions in their martensites lattice firmly concludes due to the formations of the B19’ martensites against B19 martensites as observed in as-solutionized and aged for 4 h sample. The soft nature of the B19 martensites imports less exothermic energy (J/g) and fewer distortions in their corresponding lattice.

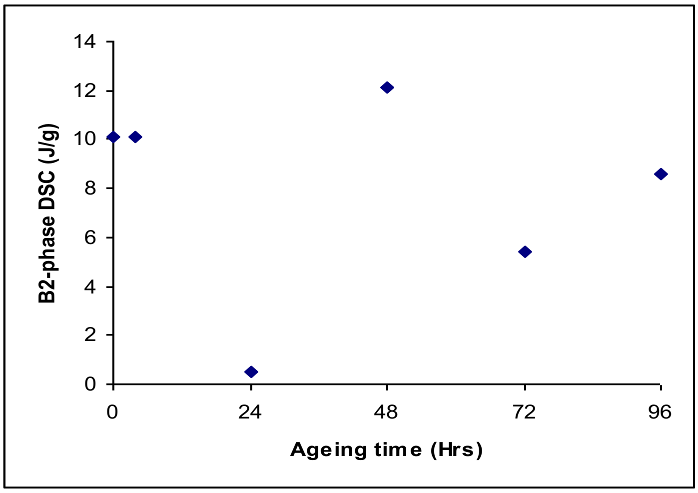

Fig.10. Changes in the DSC (J/g) values of the B2 phase with respect to the ageing time.

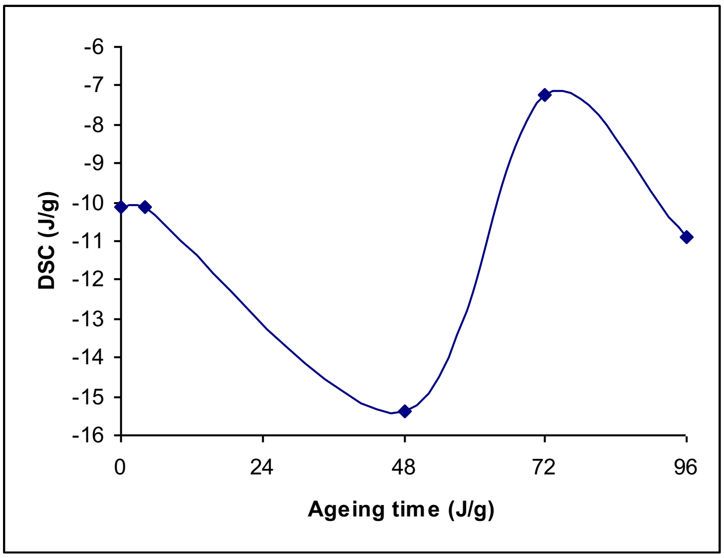

Fig.11. Exothermic energy evolved by the sample with respect to the ageing time

The characteristics of the thermal hysteresis η=Af-Ms with respect to the ageing time was shown in Fig. 12 Thermal hysteresis observed in solutionized and aged for 4 hrs samples were very low in value precisely 26K. It reflects the soft nature of B19 orthorhombic martensites [5]. However, encountering of the B19' martensite will lead to the increasing η values near about 35ºC [5], it reflects the range of lattice distortions observed in B19' martensites is more than B19 martensites. Further increasing ageing time beyond 48 hrs was resulted increasing η values. It is lucid from the above discussion that ageing time beyond 48 hrs exhibits B19' monoclinic martensite than B19 martensite observed in as-solutionized conditions. Therefore, it is proven that lower ageing time upto 4 h follows B19↔B2 phase transformations and higher ageing time 96 h follows B19'↔B2 phase sequences and intermediate time aged sample follows B19↔B19'↔B2 transformation (aged for 48 and 72 h samples).

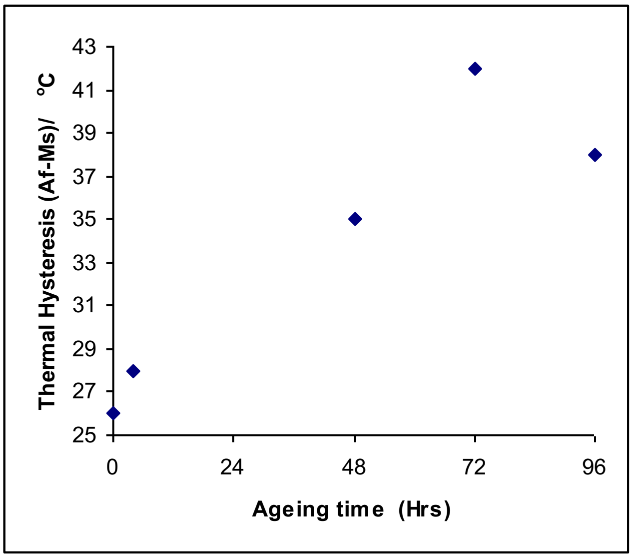

Fig. 12. variations of thermal hysteresis $\eta=A_f-M_s$ with respect to the ageing time (hrs)

5. Conclusions

1. The above discussion was proven that TiNiCu shape memory alloys were unstable at ageing temperature of 150ºC.
2. The martensitic phase transformation sequences observed in this present study as follows: As-solutionized and aged for 4 hrs samples B19↔B2; Aged for 24 h, 48h and 72 h B19↔B19'↔B2 and pro-longed aged sample for 96 hrs- B2↔B19'.
3. The strong diffraction peaks were identified at 42.28º (2θ) corresponds to the B19 orthorhombic martensites with (020) plane in NiTi aged at 150ºC for 24 hrs
4. It is clear from X-ray diffraction phase analysis formation of equilibrium Ni_3Ti precipitates reaches maximum counts with (020) plane in aged for 48 h sample as compared to the aged for 24 h sample.
5. The high DSC values (J/g) of the exothermic peak was recorded in aged for 48 hrs samples was concluded formations of the B19' martensites along with B19 martensites.

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