Materials and Manufacturing Processes Vol. 12, No. 6, 1093-1105, 1997

Thermomechanical Study of Combustion Synthesized Ti-Ni Shape Memory Alloy

F. M. H. Zarandi
Department of Metallurgical Engineering
Sharif University of Technology
Tehran, Iran 11365-9466

K. Sadrnezhaad
Janbazan Engineering and Medical Sciences Research Institute
Tehran, Iran 19615-616

Abstract

Thermal explosion mode of self-propagating high-temperature synthesis by which time and energy can be saved and the cast product has the least interstitial contamination and the greatest homogeneity is used to successfully produce the Ti-Ni shape memory alloy. The specimens after hot and cold rolling are solution treated and aged. M_s and T_R have their maxima at ageing temperatures of 500 and 450°C, respectively. These temperatures rise with the Ni content. The rate of rise of M_s and T_R in aged specimens depends on the composition so that in the Ti-50.33 at.% Ni alloy, M_s is greater than A_s while in the Ti-50.23 at.% Ni alloy, the reverse is observed. The rate of variation of M_s and A_s decreases with increasing ageing temperature when solution treatment is followed by cold working. Under this condition, T_R is greater than that for the specimens without cold working. Cold working strains produce a nonuniform effect on M_s and T_R in aged specimens.

1.0 Introduction

There has been increasing interest in materials that are capable of remembering their original shape, during past two decades. An important example is Nitinol, a Shape Memory Alloy (SMA) that principally contains the intermetallic compound TiNi (1). Plastically deformed Nitinol reverts, for example, back to its original shape if it is heated up to a temperature above the martensite to austenite transformation temperature (A_s).

Shape Memory Effect (SME) is generally due to the elastic accommodation of the thermoelastic phase in the austenite parent phase (2, 3). This effect occurs in stoichiometric TiNi which is called 55-Nitinol because it contains 55 wt% nickel (or 50 at.% Ni). Deviation from 55-Nitinol towards Ni-rich compound yields a second group of alloys in which fatigue life, strength and SME can considerably be improved through heat treatment. The martensitic transformation temperature depends on chemical composition, thermomechanical treatment and method of fabrication. Factors that influence this transformation have extensively been investigated. Studies on the effect of annealing followed by cold working and ageing have, for example, shown that the normal martensitic transformation can be preceded by formation of a rhombohedral phase that can be produced by occurring a separate transformation from the B2 parent phase (4, 5).

Such a two-stage transformation behavior is usually associated with decrease of the martensitic start transformation temperature, M_s, as a consequence of formation of dislocations or precipitates during low temperature heat treatment (6,7). It has been shown that in alloys containing more than 50.6 at.% Ni, three phases of Ti_3Ni_4, Ti_2Ni_3 and $TiNi_3$ can successively be separated due to diffusional transformation during ageing (8-11):

$$ß_0 \rightarrow ß_1 + Ti_3Ni_4 \rightarrow ß_2 + Ti_2Ni_3 \rightarrow ß_3 + TiNi_3$$

where $ß_0$ is the original supersaturated Ni-rich alloy (at room temperature), $ß_1$ is the composition of the matrix in equilibrium with Ti_3Ni_4 and so on.

The Ti_3Ni_4 precipitate is the most useful secondary phase for inducing memory properties in the TiNi alloy (8,11). Regarding this discussion, it has been reported that an optimum treatment to get better practical characteristics is to anneal or age the alloy at 500°C or less (7, 12, 13).

Although considerable achievements have so far been obtained in production and properties of TiNi alloys, there are still controversies on how to precisely achieve the required SME characteristics. An important issue is, for example, the choice of the alternative production methods as they affect the chemical composition. It is, therefore, necessary to choose a well qualified way to maintain the composition within ± 0.025% of the specified value in order to achieve a specific transformation temperature (1).

Conventional techniques for production of Nitinol are electric arc melting and high frequency vacuum induction melting of the carefully weighed constituents, followed by casting and thermomechanical processing of the final product. The arc melting process must be repeated several times in order to achieve an acceptable homogeneity. In vacuum induction melting, the contamination coming from the graphite crucible is generally inevitable. The cast material frequently exhibits micro-structural segregation which must be eliminated by mechanical working and heat treatment.

An alternative method to produce Nitinol is first to sinter and then to extrude a mixture made of titanium and nickel powders. Although this process results in production of a dense component, the shape memory response of the product is not as good as that obtained in the cast and worked piece.

Combustion synthesis, also called self-propagating, high-temperature synthesis (SHS), is a novel process for production of Nitinol (14). This method lends a new approach to the production of high technology, high temperature materials and intermetallic compounds. Once reaction between the powdered reagents is ignited, it is sufficiently exothermic and it becomes self-sustaining. Since the processing time is very short (several seconds to a few minutes), combustion synthesis can save time and energy. In addition, its cast product is favorably homogeneous and highly clean as compared to the conventional methods. Considering the increasing use of TiNi shape memory alloy in improving technology and materials (15-17), combustion synthesis can be expected as a preferable method of the alloy production and its product should be studied in more detail.

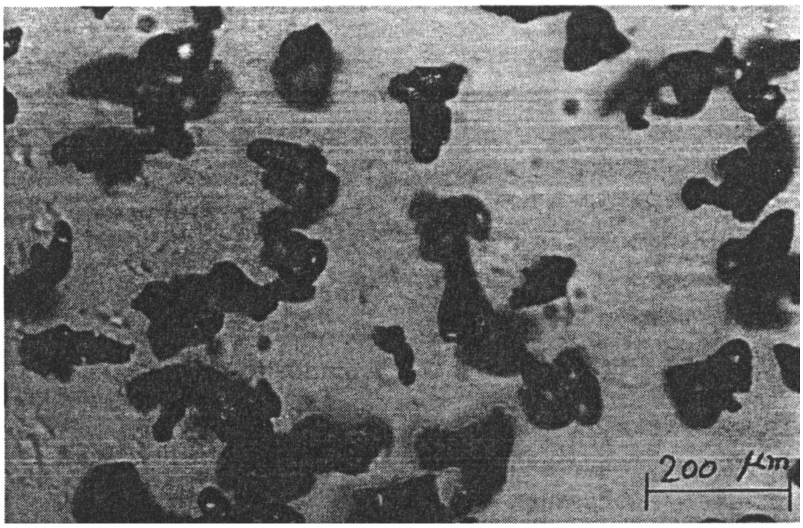
The purpose of this investigation is to study phase transformation occurring in combustion synthesized samples as compared to those associated with the conventional methods. Ni-rich alloys with small differences in the chemical composition are selected in order to obtain the sensitivity of the transformation temperatures to the nickel content of the specimens. The ageing temperatures are chosen within a range (350-600°C) so that a maximum change can be obtained in the transformation temperatures of the samples.

2.0 Experimental Procedure

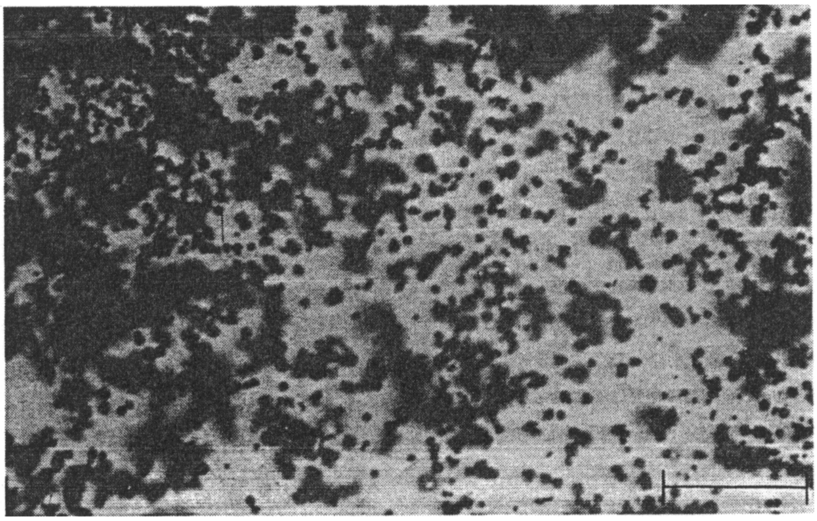
Irregularly shaped titanium powders with purity of 99.9% and less than 120 μm in size were mixed with spherically shaped nickel powders with purity of 99.8% and averaged 15 μm in size. A magnified picture of the powders is shown in Figure 1. Three samples with compositions of 50.03, 50.23 and 50.33 atomic percent nickel were produced by 15 minutes tumbling of the powder mixtures. With no addition of any binder, the samples were subsequently compacted in a rectangular mould in order to obtain a specimen with dimensions of 51x6x6 mm^3 and density of 66±1% of the theoretical TiNi intermetallic compound. Each specimen was produced at room temperature and weighed 10 grams.

The specimens were placed in a tube furnace under flowing argon and were combustion synthesized in less than a minute. The cast product, that a typical micrograph of cross section has been shown in Figure 2, was then rolled at 850°C up to 1 mm in thickness. Cold rolling further decreased the thickness of the samples to approximately 0.4 mm after removing the oxidized layer formed on the surface of the specimens.

All specimens were solution treated for 1 hr at 1000°C under vacuum and then water quenched. Ageing was carried out at 350 to 600°C for different periods of time. Transformation temperatures were then measured by the resistometery method (18).



(a)



(b)

Figure 1: Powders of (a) Ti and (b) Ni used to produce Nitinol.

3.0 Results and Discussion

3.1 Effect of Ageing Temperature on Transformation Temperatures

In solution treated specimens M_s goes up with increasing the ageing temperature up to 500°C and then decreases with a further rise of the ageing temperature (Figure 3). Similar results have previously been obtained by T. Honma et al. (13) for a Ti-51 at.% Ni alloy. No explanations have however, been given

Figure 2: A typical micrograph of combustion synthesized Ti-50.03 at.% Ni alloy. TiNi matrix and eutectic composition of $TiNi-TiNi_3$.

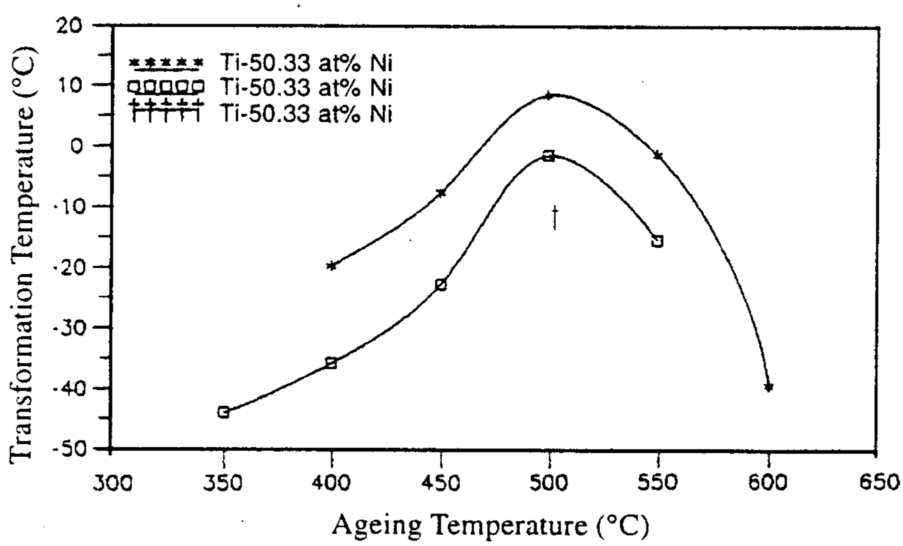


Figure 3: Effect of ageing temperature on M_s temperature. All samples were aged for 1 hr after solution treating at 1000°C for 1 hr. (One data for 50.03 at.% Ni).

on the shape of the plot especially after ageing at 500°C.

It has previously been found that two metastable phases of Ti_3Ni_4 and Ti_2Ni_3 can be formed during ageing of TiNi supersaturated phase (19, 20). Longer ageing, however, results in transformation of these phases into the stable $TiNi_3$ phase. Simultaneous existence of the metastable phases have been proved by Xie et al. in a Ti-51.8 at.% Ni alloy at 600°C (20). It has also been shown that the ageing

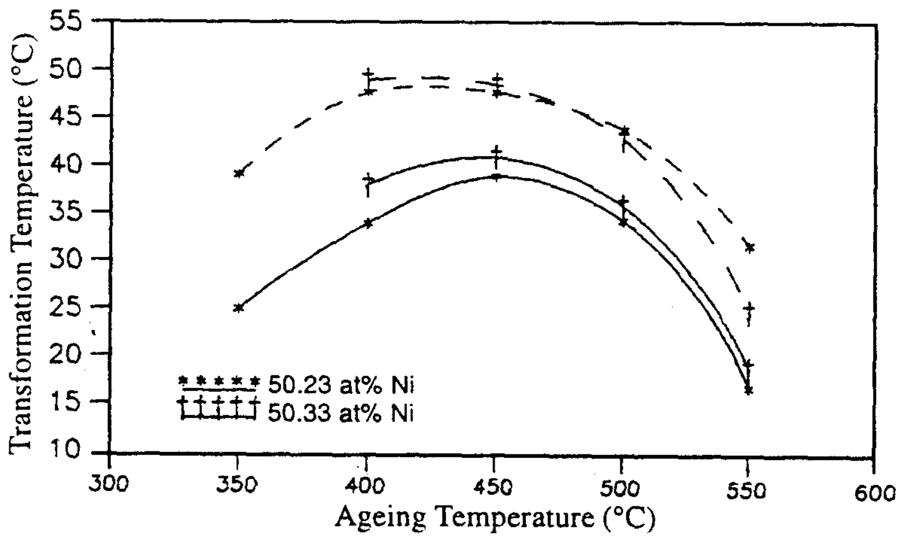


Figure 4: T_R(solid line) and T_I(dashed line) temperatures against the ageing temperature for an ageing time of 1 hr after solution treating at 1000°C for 1 hr.

results in growth of Ti_2Ni_3 particles and consumption of Ti_3Ni_4 phase (19-21).

TEM observation have shown that Ti_3Ni_4 precipitates have finer distribution (greater number in a specified space) than Ti_2Ni_3 precipitates (20). On the other hand, low temperature ageing results in formation of Ti_3Ni_4 as the first transition phase before $TiNi_3$ formation (10), at the fastest transformation rate associated with the highest nucleation rate. With regard to these points and a typical TTT diagram describing ageing behavior of the alloy (22), it can be inferred from the experimental results shown in Figure 3 that up to 500°C, Ti_3Ni_4 particles precipitate in the matrix and M_s rises due to removal of Ni from the parent phase.

It has been reported that the excess nickel atoms in the supersaturated TiNi parent phase are substitutional defects lowering M_s (23). Faster precipitation caused by increasing the ageing temperature results in faster removal of Ni from the parent phase and a consequent faster increasing of M_s. At higher ageing temperatures, in addition to Ti_3Ni_4 particles, Ti_2Ni_3 precipitates will also separate from the matrix. At temperatures lower than 500°C, smaller nucleation rate causes slower reduction of Ni in the parent phase and a consequent slower increase in M_s. This is why a maximum is observed in the plot of M_s against the ageing temperature shown in Figure 3.

It has already been demonstrated that the rate of nucleation of precipitates increases with increasing Ni content of the specimens (8). The rate of removal of Ni from the matrix and the transformation temperature M_s both increase with increasing Ni content of the specimen, as shown in Figure 3.

Figure 4 shows variations of T_R against the ageing temperature. Fine precipitates formed upon ageing introduce coherency stresses at interface with the matrix and cause a rhombohedral phase (R-phase) transformation to take place before the martensitic transformation. It has been confirmed earlier that Ti_3Ni_4 forms coherent particles with the matrix (11). It can, therefore, be supposed that up to 450°C, the coherency stresses increase at the Ti_3Ni_4-matrix interface and cause an increase in T_R.

Since the rate of growth of the precipitates depend on the ageing temperature, the coherency is destroyed above 450°C faster than below 450°C. At temperatures above 450°C, T_R decreases, therefore decreasing the stress at the interface. The appearance of the dislocation at the interface between grown Ti_3Ni_4 and matrix has proved semicoherency of the precipitates with the matrix (20).

The rate of nucleation increases with the Ni content of the specimens. Because of the faster growth of the precipitates, the T_R increases faster in the alloys with higher nickel content. Similar results have been obtained for the starting temperature of incommensurate phase transformation (T_I), the phase transformation that occurs because of the excess nickel atoms in the TiNi supersaturated parent phase (20, 24). It will be shown later that ageing at 600°C eliminates both R-phase and the incommensurate phase transformation. This means that the martensitic phase transformation occurs before the other two.

3.2 Effect of Ageing Time on the Transformation Temperatures

Increasing the ageing time results in the coarsening of the precipitates (20) and greater reduction of the Ni content of the matrix. Figure 5 shows the effect of the ageing time at 450°C for two compositions. The slope of M_s versus time is greater at shorter times than at longer times and tends to a horizontal curve at very long times.

It is important to notice that there is no transformation hysteresis in Ti-50.33 at.% Ni alloy. This is probably due to the lack of any interstitial contamination in combustion synthesized specimens. Similarly one would expect that in Ti-50.23 at.% Ni alloys, M_s will be equal to A_s at longer times.

Similar results are observed in Figure 6 for the samples at 500°C. Lowering Ms in Ti-50.33 at.% Ni relative to Ti-50.23 at.% Ni after two hours of ageing can be due to the higher rate of depletion of Ni from the matrix during growth of precipitates. The transformation temperature is controlled by the nucleation of precipitates at the earlier times (short ageing times), however the growth of the precipitates is much more effective at the longer times. This is why the results are reversed after 2 hrs of ageing. The Ti_3Ni_4 phase grows with increasing ageing time. Increasing coherency stress results in increasing T_R (Figure 7). Since coherency is destroyed faster in alloys with greater Ni content, the rate of increase of T_R in Ti-50.23 at.% Ni is more than that in Ti-50.33 at.% Ni. This suggests that in Ti-50.33 at.% Ni, at short times, the size of the precipitates and the stresses at the interfaces are lager than in Ti-50.23 at.% Ni, but at long times, the stresses due to the coherent interface are smaller and the two curves intersect.

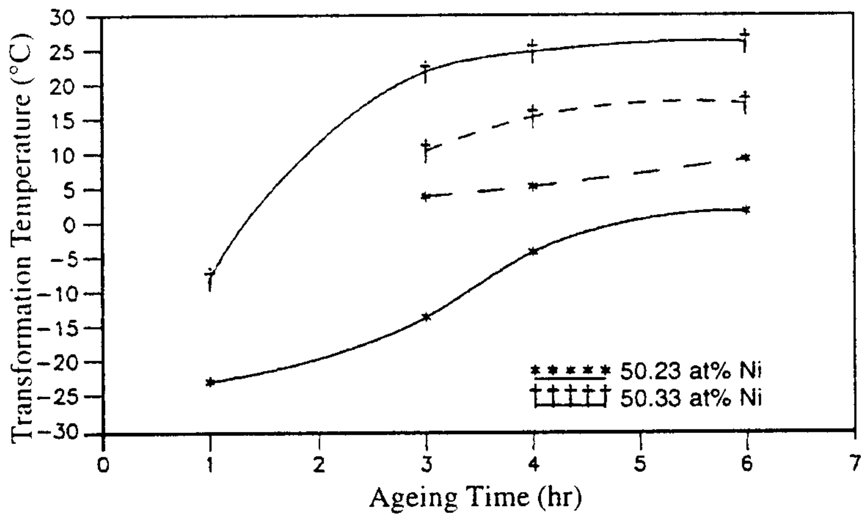


Figure 5: Effect of ageing time on M_s(solid line) and A_s(dashed line) temperatures. These specimens were aged at 450 °C after solution treatment at 1000°C for 1 hr.

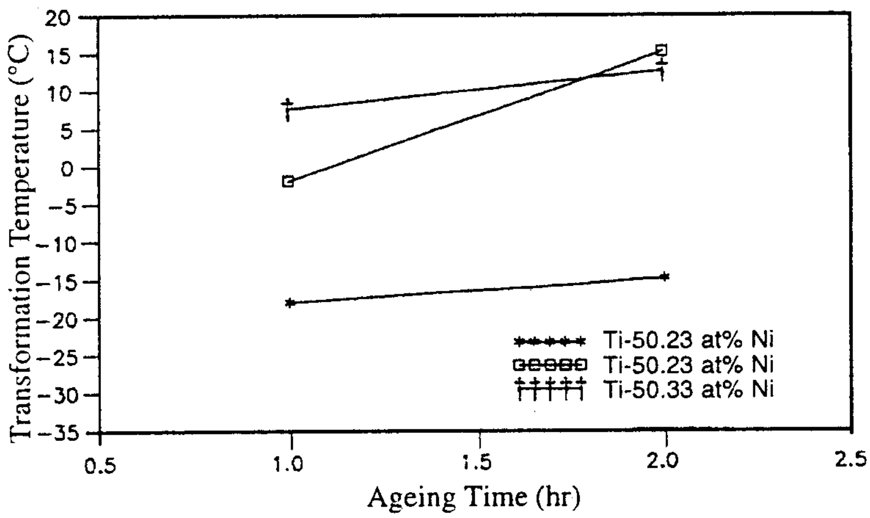


Figure 6: Effect of ageing time on M_s temperature. Specimens were solution treated at 1000°C for 1 hr and then aged at 500°C.

3.3 Effect of Cold Working on Transformation Temperatures

Figure 8 shows the variations of M_s and A_s with the ageing temperature in solution treated, 40% cold rolled (reduction in thickness) specimens. Transformation temperatures of this class of alloys are controlled by two mechanisms; (a) precipitation and (b) forming of dislocation cells. Up to 500°C, Ti_3Ni_4 is formed and dislocations are so arranged as to reduce internal stresses. Since the dislocation lattice is not completely destroyed, M_s is lower than that of specimens with no cold working. Dislocations due to cold working act as a

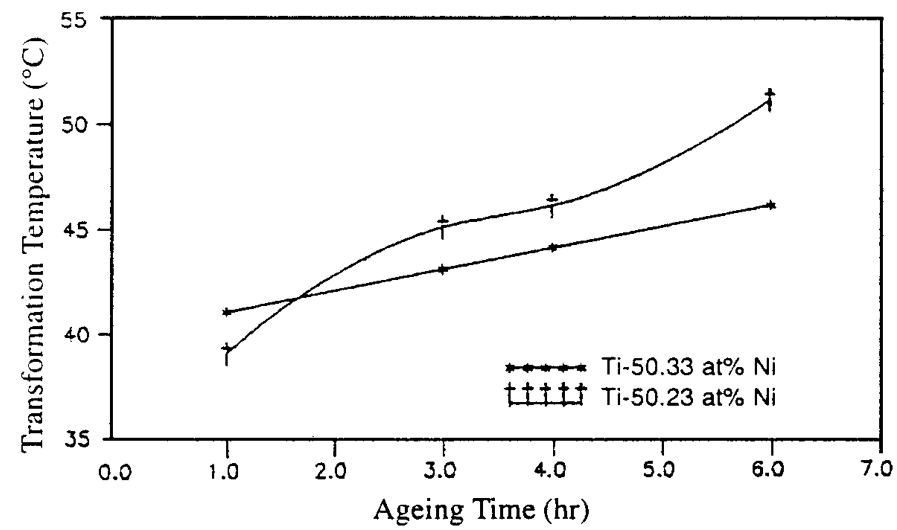


Figure 7: Effect of ageing time on T_R temperature. Specimens were solution treated at 1000°C for 1 hr and then aged at 450°C.

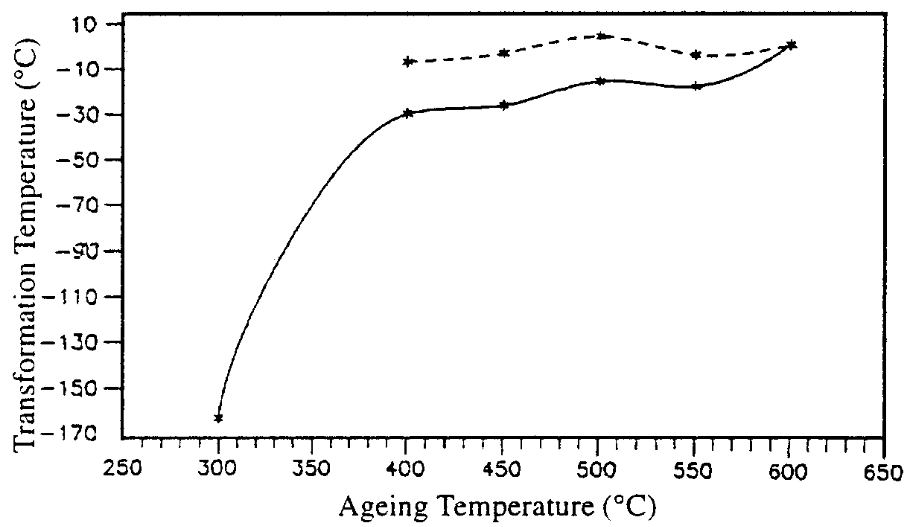


Figure 8 : Effect of ageing temperature on M_s (solid line) and A_s (dashed line) temperatures in solution treated and 40% cold worked Ti-50.23 at.% Ni alloy. Ageing time is 1 hr.

barrier to the formation of martensite plates and are responsible for the stabilization of the high temperature parent phase (25, 26).

Nucleation of precipitates up to 500°C is probably independent of the presence of dislocations. Between 500 and 550°C, the types of precipitates vary and the dissolution of nickel in the matrix is started and therefore M_s decreases. On the other hand, with increasing ageing temperature, the rate of recovery increases and M_s must therefore be increased too. These mechanisms have the opposite

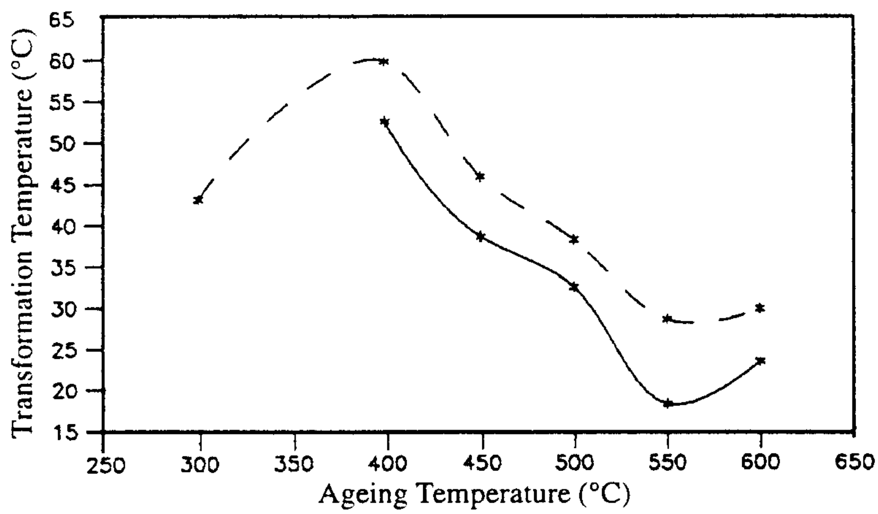


Figure 9: Effect of ageing temperature on T_R(solid line) and T_I(dashed line) temperatures in solution treated and 40% cold worked Ti-50.23 at.% Ni alloy. Ageing time is 1 hr.

effects on M_s, and result in a lowering of the rate of the decreasing of M_s relative to those specimens that are aged without any cold working.

With further increase in ageing temperature to 600°C, M_s increases again. Thus, we can infer that at 600°C, the precipitates use the concentrated dislocation sites as nucleation sites. Therefore, the rate of nucleation at 600°C is more than that at 550°C, and with increasing rate of removal of nickel from the matrix, M_s increases. This result is controversial when compared with that of Fillip et al., who assumed that the precipitates dissolved at 600°C and hence the M_s decreased (27).

A dislocation density increase results in an increase in the difference between M_s and A_s. This is because of the increases occurring in the energy necessary for the moving of the martensitic variants with cold working strain (28). Decreasing the transformation hysteresis is therefore due to the decrease in the density of dislocations (Figure 8).

The variation of T_R with the ageing temperature in solution treated and 40% cold worked specimen are shown in Figure 9. R-phase transformation is started at 400°C. Since at this temperature, T_R is higher than that in specimens with no cold working, the R-phase transformation is thus affected by stresses due to the dislocation. With increases in the aging temperature, T_R decreases so that above 450°C, T_R is preferably controlled by the coherency stresses, as can be inferred from Figure 4. At 600°C, two mechanisms are active : (a) recrystallization (29) and (b) precipitation. Both mechanisms result in decreasing the internal stress. However, R-phase transformation must be affected by dislocation rearrangement here because in specimens without cold working, R-phase

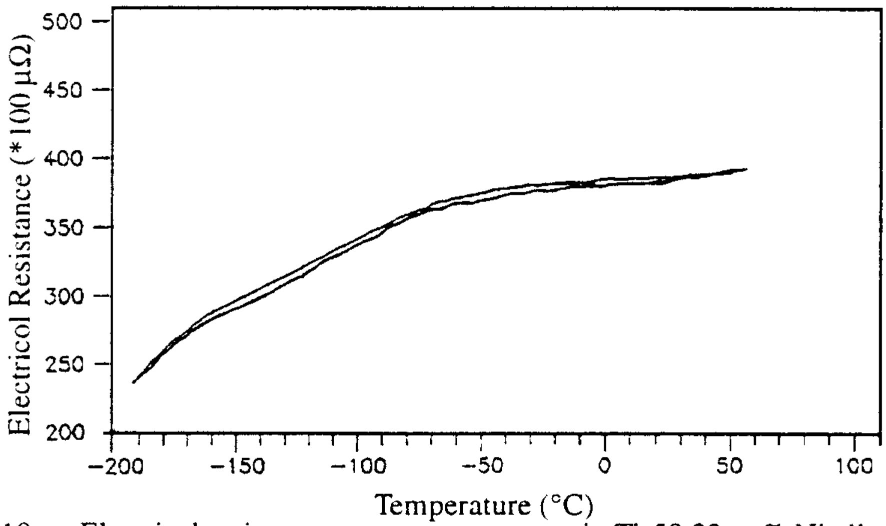


Figure 10: Electrical resistance versus temperature in Ti-50.33 at.% Ni alloy aged for 1 hr at 600°C after 1 hr solution treating at 1000°C.

transformation does not take place at 600°C (Figure 10). Since R-phase transformation is preceded by an initial disordering in the parent phase, or incommensurate phase transformation, and ageing has a similar effect on these two transformation temperatures, similar results are obtained for T_I (Figure 9).

4.0 Conclusions

The results of this study are summarized as follows:

1. In solution treated and aged specimens, M_s increases with increasing Ni content of the Ti-Ni alloy, within the composition range studied in this research (50.03 - 50.33 at.% Ni).
2. M_s and T_R reach their maxima at the ageing temperatures of 500°C and 450°C, respectively.
3. Under the same ageing treatment, no hysteresis is observed in Ti-50.33 at.% Ni alloy, while the reverse is true for Ti-50.23 at.% Ni alloy.
4. Cold working decreases the rate of rise of M_s.
5. Ageing after cold working results in occurring of R-phase transformation at ageing temperature of 600°C.
6. Combustion synthesized alloy are cold rolled more readily than those produce through the conventional methods.

5.0 References

1. Goldstein, D. et al., U. S. Patent 4,282,033, (1981).

2. Otsuka, K., T. Sawamura, K. Shimizu, and C. M. Wayman, Metallurgical Transactions, Vol.2, p.2583-2588, (1971).

3. Olson, G. B. and M. Cohen, Scripta Metallurgica, Vol.9, p.1247-1254, (1974).

4. Miyazaki, S. and K. Ostuka Metallurgical Transactions, Vol.17A, p.53-63, (1986).

5. Nishida, M. and C. M. Wayman Metallography, Vol.21, p.255-273, (1988).

6. Favier, D., Y. Liu, and P.G. McCormick, Scripta Metallurgica, Vol.28, p.669-672, (1993).

7. Todoroki, T. and H. Tamura, Transactions of Japan Institute of Metals, Vol.28, p.83-94, (1987).

8. Nishida, M. and T. Honma, Scripta, Metallurgica, Vol.18, p.1293-1298, (1984).

9. Nishida, M., C. M. Wayman, and T. Honma, Scripta Metallurgica, Vol.18, p.1389-1394, (1984).

10. Nishida, M., C. M. Wayman, and T. Honma Scripta Metallurgica, Vol.20, p.983-987, (1985).

11. Nishida, M. et al., Scripta Metallurgica, Vol.20, p.899-904, (1986).

12. Nishida, M. and T. Honma, Scripta, Metallurgica, Vol.18, p.1299-1302, (1984).

13. Honma, T. et al., U.S. Patent 4,707,196, (1987).

14. Yi, H. C. and J. J. Moore, Scripta Metallurgica, Vol.22, p.1889-1892, (1988).

15. Zarandi, F. M. H. and K. Sadrnezhaad, A study of TiNi shape memory alloy applications (internal report), Department of Metallurgical Engineering, Sharif University of Technology, Tehran, Iran 11365-9466, September, (1995).

16. Furuya, Y., A. Sasaki, and M. Taya, Materials Transactions of Japan Institute of Metals, Vol.34, No.3, p.224-227, (1993).

17. Yamada, Y., M. Taya, and R. Watanabe, Materials Transactions of Japan Institute of Metals, Vol.34, No.3, p.254-260, (1993).

18. Hanlon, J. E., S. R. Butler, and R. J. wasilewski, Transactions of the Metallurgical Society of American Institute of Mining, Metallurgical, and Petroleum Engineering (AIME), Vol.239, September, p.1323-1326, (1967).

19. Nishida, M., C. M. Wayman, and T. Honma, Metallurgical Transactions, Vol.17A, p.1505-1515, (1986).

20. Xie, C. Y., L. C. Zhao, and T. C. Lei, Scripta Metallurgica, Vol.23, p.2131, (1989).

21. Nishida, M. and C. M. Wayman, Metallurgical Transactions, Vol.18A, p.785-799, (1987).

22. Miyazaki, S. and K. Ostsuka, The Iron

and Steel Institute of Japan (ISIJ) International, Vol.29, No.5, p.353-377, (1989).

23. Wasilewski, R. J. et al., Metallurgical Transactions, Vol.2, p.229-238, (1971).

24. Zengxing, T., Proceedings of International Symposium on Shape Memory Alloys, China Academic Publisher, Beijing, p.187-192, (1986).

25. Perkins, J., Metallurgical Transactions, Vol.4, p.2709-2721, (1973).

26. Miyazaki, S., et al., Acta Metallurgica, Vol.34, No.10, p.2045-2051, (1986).

27. Fillip, P., J. Rusek and K. Mazanec, Materials Science and Engineering, Vol.A141, p.L5-L8, (1991).

28. Melton, K. N., Engineering Aspects of Shape Memory Alloys, T. Duerig K. Melton, D. Stoeckel, and C.M. Wayman, eds., Butterworth, London, p.21, (1990).

29. Goldstein, D., L. Kabacoff and J. Tydings, Journal of Metals, Vol.39, No.3, p.19-26, (1987).