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Original Paper

Addition of Interstitial Elements to Ti_2Ni Intermetallic Compound and Increase of Viscosity

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Effect of interstitial elements in Ti_2Ni intermetallic compound has been investigated. Added interstitial elements are oxygen, nitrogen, and carbon. Although Ti_2Ni contains around 14 at% oxygen without changing its crystal structure, the intermetallic compound is found dissolved a smaller amount of nitrogen, and carbon. The excess interstitial elements form titanium carbide and nitride. As mealy nitrogen content increased, we observed a substantial increase of viscosity at the fluid metallic compound under argon arc melting process. The effects of interstitial elements were estimated by X-ray powder diffraction method with Rietveld analysis, grain structure analysis, electric resistivility measurement, and density measurement. We quantitatively analyzed series of crystal structure between Ti_2Ni and Ti_4Ni_2O. Although slight anomalous change of resistivility was observed, sufficient physical property changes were not obtained to explain the rapid increase of viscosity with nitrogen addition.

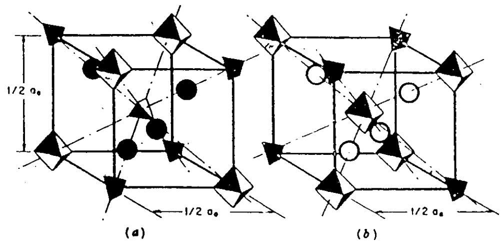
key Words: viscosity, intermetallic compound, Ti_2Ni, crystal structure, nitrogen, carbon, oxygen, interstitial element

I. Introduction

Effect of interstitial elements has been an important subject in material science. Especially in titanium alloy many light elements are soluble into the primary phase without crystal structure modifications. Usually we do not expect drastic changing of material characteristic, such as hardening, resistivility, and elastic modulus and so on, with interstitial element additives, since most of the principal characteristics are based on its crystal structure. However, surprisingly in this experiment a substantial increase of viscosity was observed with added nitrogen.

In this paper we have investigated the effects of interstitial elements, such as oxygen, nitrogen, and carbon to the Ti_2Ni intermetallic compound. As shown in Figure 1, the Ti_2Ni intermetallic compound forms a continuous solid solution until at most 14 at% of oxygen[(1)-(3)], which is the Ti_4Ni_2O phase, in interstitial sites of the crystal. Since the crystal structure does not change between Ti_2Ni and Ti_4Ni_2O and since oxygen is one of the light elements, they are indistinguishable in X-ray diffraction method. G.A.Yurko, J.W.Barton, J.G.Parr, M.H.Mueller and H.W.Knott have determined crystal structure and atomic positions in both phases. However, series of crystal structure measurement between Ti_2Ni and Ti_4Ni_2O as a function of oxygen composition has not been measured to analyze the continuous effect of the interstitial element to its crystal structure. In the last ten years Rietveld analysis(5) has been strongly developed, and has performed quantitative crystal structural analysis from X-ray powder diffraction data. This method allows us to obtain more accurate crystal parameters, such as lattice constants, atomic positions and atomic occupation ratio, than previous works. It is important to estimate crystal structure change with oxygen content in the more efficient method.

Secondary, the solubility and the effect of other interstitial atoms; nitrogen, and carbon, was analyzed. Since oxygen interstitial site preserves certain capacity in the crystal structure, other light elements have possibilities to be dissolved in the intermetallic compound. Although in nitrogen we did not observe the same solubility as oxygen, substantial increase of viscosity was confirmed with increase of the additive interstitial. Since interstitial elements reduce free space in a crystal lattice, it is natural that viscosity slightly increases. However, in nitrogen the viscosity of Ti_2Ni increased rapidly and in case of the other light elements any deformation was not observed. In order to account for the anomous effect of nitrogen, we analyzed some material characteristics. However, sufficient characteristic changes was not observed except electric resistivility. The increase of viscosity suggests that some light elements might help to form amorphous metals with their viscosity increases.



Crystallographic subcell arrangement(1) in (a) Ti_2Ni (b) Ti_4Ni_2O

	Ti_2Ni	Ti_4Ni_2O
System	Cubic	〃
Space Group	Fd3m	〃
Atoms per Unit Cell	96	112
Ti (48f)	(x, 1/8,1/8)	〃
Ni (32e)	(y, y, y)	〃
Ti (16c)	(0, 0, 0)	〃
O (16d)		(1/2,1/2,1/2)

Fig. 1 Crystal Structure and crystal parameters of Ti_2Ni

2. Experimental

2.1 Sample preparation

Ti_2Ni intermetallic compound and its light element (oxygen, nitrogen, carbon) added specimens were prepared in the following procedures. Intended compositions of the prepared samples are; (1) $Ti_4Ni_2O_y$: y = 0.00, 0.25, 0.50, 0.75, 1.00, (2) $Ti_4Ni_2N_y$: y = 0.00, 0.20, 0.40, 0.60, 0.80, 1.00, (3) $Ti_4Ni_2C_y$: y = 0.00, 0.20, 0.40, 0.60, 0.80, 1.00 in terms of molar ratio. Ti_2Ni was prepared from pure metals and each interstitial element was added as a form of titanium oxide, nitride or carbide. Titanium (quoted as 99.5% pure excluding gaseous species), Nickel (quoted as 99.9% pure), and high purity compound of titanium dioxide, titanium nitride and titanium carbide were weighted into 20g of the above compositions. We melted all the specimens with an argon arc furnace and in the furnace we used a tungsten electrode and a water-cooled copper crucible. The pressure of argon gas atmosphere was around 700 torr. Since the melting point of Ti_2Ni intermetallic compound is 1257 K, we can supply sufficient heat from the arc furnace to melt the specimens.

The melting process was repeated five to eight times with changing their position to prepare homogenized samples. Obtained samples were cloth polished with 0.3 μm diamond paste. They were etched with typical etching fluid (60% ethyl alcohol, 10% nitric acid, 1% fluoride hydride, and water), and grain structures were observed with optical microscopy.

2.2 Rietveld analysis of powder X-ray diffraction pattern

Powder samples of X-ray diffraction measurement were prepared by crashing bulk samples in stainless steel mortar. Fine grains with a diameter of less than 70 μm was only selected by mesh to reduce grain size effect of X-ray analysis. Employed X-ray apparatus was step-scanning type with high intensity beam (Cu, 50 kV, 100 mA). Measurement condition was 0.02 degree/step for 5 seconds holding time.

Rietveld analysis was performed assuming the following conditions. All phases of Ti_4Ni_2X (X=O,N,C) were the same Fd3m space group (No. 227 origin choice 2[4], face-centered cubic) as Ti_2Ni. The interstitial elements in the Ti_4Ni_2X phase were placed at the same position of oxygen in the Ti_4Ni_2O phase. The occupation ratios of atoms were identical for equivalent sites. The unit cells of Ti_2Ni and Ti_4Ni_2X are composed of 96 and 112 atoms respectively. The lattice constant of the cubic cell (d_0) was about 1.132 nm with following atomic position parameters; Ti(48f); (x,y,z) = (x,1/8,1/8), Ni(32e); (x,y,z) = (y,y,y), Ti(16c); (x,y,z) = (0,0,0), X(16d); (x,y,z) = (1/2,1/2,1/2) (X=O,N,C). By M.H.Mueller and H.W.Knott[3] initial crystal parameters were determined from the Ti_4Ni_2O measured; these are d0=11.32, x=0.8118, y=0.2149. The overall thermal parameter was fixed 0.1 and random orientation was assumed. The occupation ratio was initiated to be the same as the composition of batch metals. The TiN and TiC phase were Fm3m space group (No. 225[4], face centered cubic), with the following atomic position parameters; Ti(4a); (x,y,z)=(0,0,0), X(4b); (x,y,z)=(1/2,1/2,1/2) (X=O,N). The total sums of nitrogen and carbon ratios were fixed in those of batch metals. The modified Marquardt nonlinear least square fitting has been repeated to obtain adequate crystal parameters until integrated intensity R-factor (RI) reaches below 10.0. We also evaluated the standard deviations of the crystal parameters.

2.3 Density measurement

Densities of ϕ 20 * t5mm button shaped samples were measured in Archimedes method with chemical balance. We ignored pores inside of the specimen. The sample, hung with copper wire, was put down into water. By keeping water level at the same position, the error factor of the wire weight was canceled. The examination was repeated six times to obtain the standard deviations of the measurement.

2.4 Electric resistivity measurement

Temperature dependence of electric resistivity was measured by DC four terminal method. Copper electrodes contacted ϕ 20 * t5 mm button shaped bulk samples through indium metals. The gap between voltage terminals was 10 mm. Temperature of the specimens, monitored by alumel-chromel thermocouple, was changed from room temperature to 100 K with using a helium cryogenerator.

3 Results

3.1 Shape figures of the as-melted samples and their grain structures

The button shaped samples, which were as-melted in the argon arc furnace, are shown in Figure 2. Since the intermetallic compound was weak or brittle for thermal stress during the melting process, some specimens were broken into the half. Mealy in nitrogen added specimen, shape deformation was observed. During the arc melting process, since argon gas wind blows from the tungsten electrode to the specimen, certain wind force was applied to induce the deformation. When the pure Ti_2Ni or oxygen (or carbon) contained intermetallic compound was melted, the fluid surface was lightly moved and sample deformation was not preserved. However, when the nitrogen contained specimen was melted, since fluid state showed high viscous property, deformation remained into the solid. According to the observation results we conclude that viscosity increases with content of nitrogen.

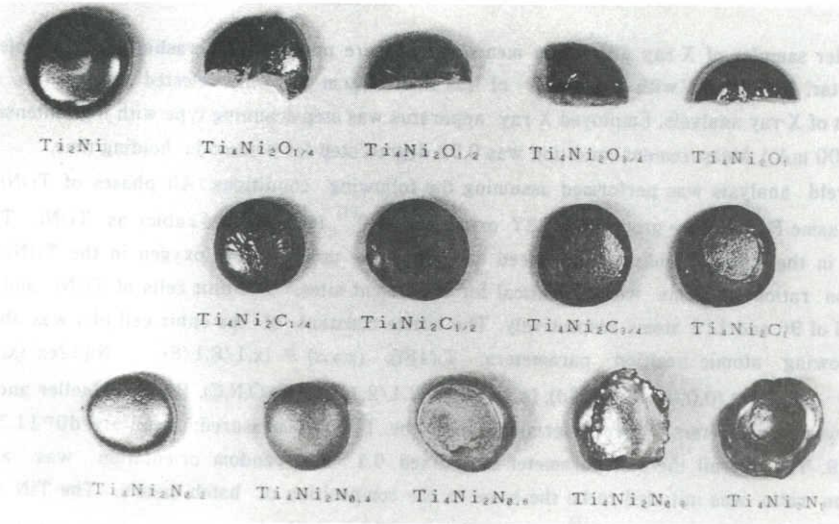


Fig. 2 Shape figures of as-melted Ti_4Ni_2X (X= O, N, C) — 10 mm

Figure 3 indicates grain structures of Ti_2Ni, Ti_4Ni_2O, Ti_4Ni_2C, and Ti_4Ni_2N intermetallic compound. Ti_2Ni and Ti_4Ni_2O grain structures show mono phase structure, and they suggest that up to 14 at% oxygen is dissolved into the Ti_2Ni phase, which was denoted in the previous paper[1]. Grain structures of Ti_4Ni_2C and Ti_4Ni_2N suggest existence of the secondary phases. The extra phases imply that carbon and nitrogen are not dissolved into the Ti_2Ni phase as much as 14 at%. According to X-ray measurement we conclude that the secondary phases are TiC and TiN. Certain amount of a Ni phase might be expected, but obvious diffraction peak was not observed.

3.2 Crystal structure analysis by X-ray measurement

For crystal structure analysis, X-ray profile fitting method, which was termed Rietveld analysis and was programmed by F. Izumi et. al.[5], was performed. Fitted X-ray profiles and differences between fitted profile and measured profile of Ti_2Ni, Ti_4Ni_2O, Ti_4Ni_2N and Ti_4Ni_2C are shown in Figure 4. The experimental X-ray profile figure was not well expressed with model function, which was mixture of Gaussian and Lorentian function. Although certain differences were existing, all of peak

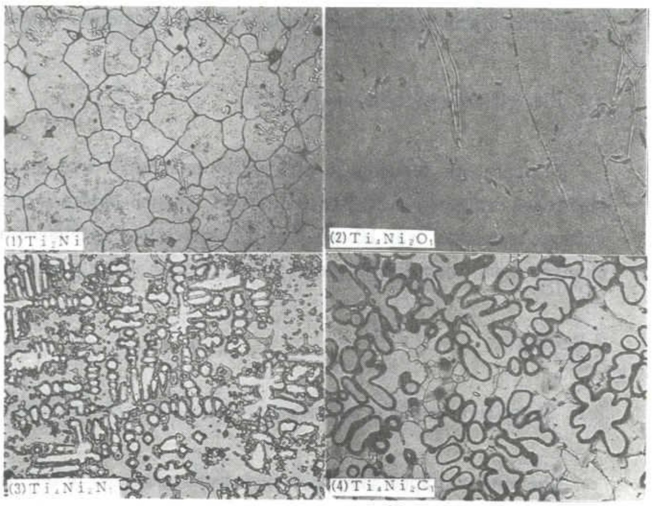


Fig.3 Crystal Structures of $Ti_4Ni_2X_{1.0}$ Intermetallic compounds (1) Ti_2Ni, (2) Ti_4Ni_2O, (3) Ti_4Ni_2N, (4) Ti_4Ni_2C

differences were existing, all of peak positions were successfully fitted. Concerning with integrated intensity R-factors, we found X-ray profiles of Ti_2Ni and Ti_4Ni_2O were well fitted rather than that of Ti_4Ni_2N. We believe that in Ti_4Ni_2N samples, since some TiN was precipitated in the Ti_2Ni phase, the ternary Ni phase made the R-factors much larger. Therefore it should be noticed that in Ti_4Ni_2N specimen Rietveld analysis involves certain error.

Figure 5 shows lattice constants as a function of molar fractions of oxygen and nitrogen. Both lattice constants indicated the maximum value at around 7% molar fraction of the interstitial element. Also Figure 6 describes atomic position changes; Ti(48f); (x,y,z) = (x,1/8,1/8) and Ni(32e); (x,y,z) = (y,y,y). The error bars indicate the standard deviations of crystal parameters. The parameters of the oxygen contained specimen exhibit linear change with increases of light elements. However, in nitrogen the parameter change did not suggest any obvious tendency.

3.3 Density and electric resistivity measurement

As exhibited in Figure 7, whereas density of $Ti_4Ni_2O_x$ (x=0 to 1) sample shows a linear increase as a function of oxygen, that of $Ti_4Ni_2N_x$ (x=0 to 1) remains constant. The results indicate that oxygen can be dissoluble in the Ti_2Ni phase up to 14 at%, and that nitrogen additive remains as the TiN phase without large solubility in the Ti_2Ni phase.

Specific resistance of the compounds; Ti_2Ni, Ti_4Ni_2O, $Ti_4Ni_2N_{0.8}$ and Ti_4Ni_2C, was denoted in Figure 8. The resistivity is not largely changed with temperature since residual resistivility, which is caused by lattice defect and impurities, is much larger than a temperature depended term. The resistivity of Ti_4Ni_2O, which is triple times larger than those of the other samples, suggests the solubility effect of oxygen. The resistivity of Ti_2Ni, Ti_4Ni_2N and Ti_4Ni_2C, which shows almost the same values, implies small solubility of nitrogen and carbon in the Ti_2Ni phase. The resistivity gradient change was observed mealy in Ti_4Ni_2N specimen around at 240 K with good reproducibility. There can be relations between high viscosity and the resistivity change, though apparent mechanisms have not been confirmed.

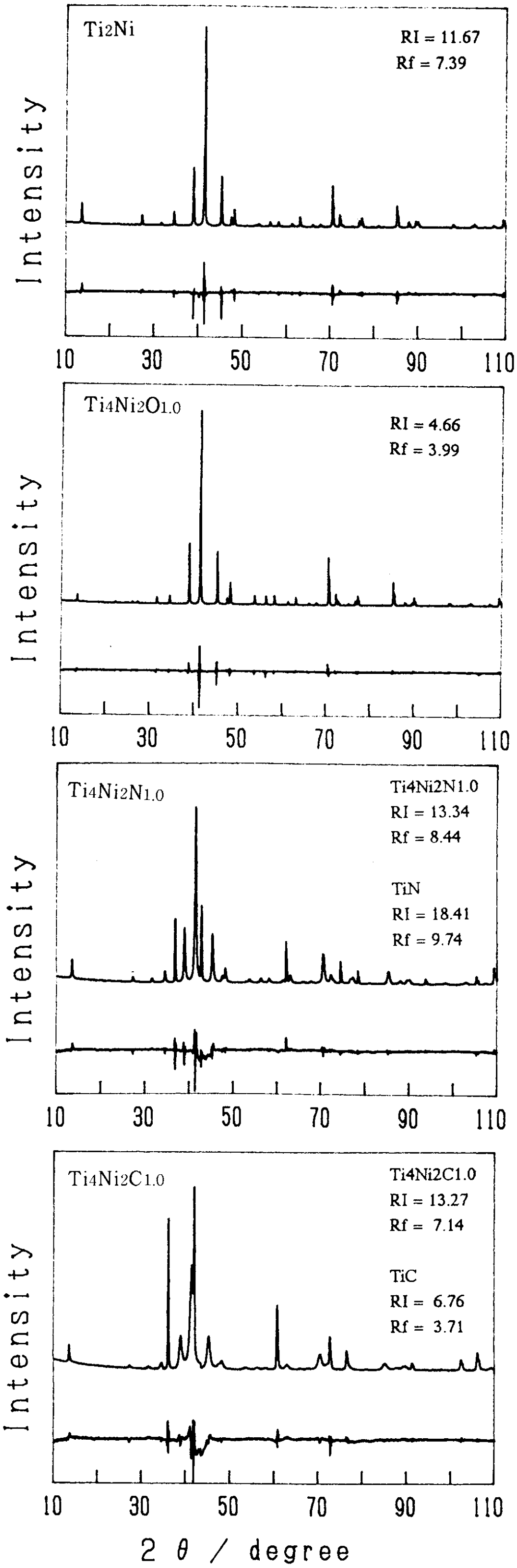


Fig. 4 Fitted X-ray profiles and differences between fitted X-ray profile and measured X-ray profile

4. Discussion

4.1 Solubility of oxygen, nitrogen, and carbon in Ti_2Ni

Concerning with the results of grain structures, X-ray and density measurement, the solubility of light elements in the intermetallic compound are determined.

(a) Oxygen solubility: The previous results[(1)-(3)] that oxygen can be soluble in Ti_2Ni until forming the Ti_4Ni_2O phase were confirmed in the investigation. With addition of oxygen the lattice constant of the unit cell increases. At 7 at% oxygen it exhibits the maximum value.

(b) Nitrogen and carbon solubility: Since a large amount of titanium nitride and carbide phases were observed in the experiments, we conclude that nitrogen and carbon atoms are not dissolved in Ti_2Ni as much as oxygen. Since good RI factors were not obtained in Rietveld analysis of $Ti_4Ni_2N_x$ and $Ti_4Ni_2C_x$ samples, the lattice parameters and the atomic coefficients are not reliable. We are studying further for the ternary phases.

4.2 Nitrogen effect in Ti_2Ni

Although nitrogen is not largely soluble in the Ti_2Ni phase, since viscosity and resistivity show considerable change, we expect the effect of nitrogen solubility. In carbon contained intermetallic compound, since any physical property changes were not observed, the secondary phases; TiN and TiC, are not thought to cause the nitrogen additive anomaly.

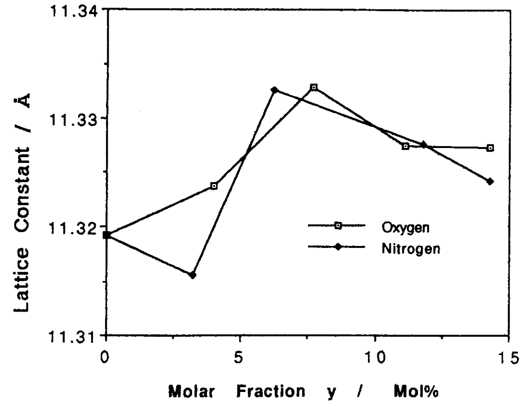


Fig. 5 Relation between Lattice Constant and Molar Fraction of Oxygen and Nitrogen in $(Ti_4Ni_2)_{100-y}X_y$ (X=O,N) Specimen

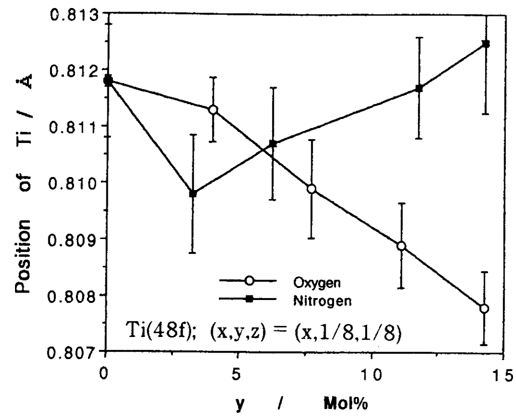


Fig. 6 (a) Relation between Titanium Position and Molar Fraction of Oxygen and Nitrogen in $(Ti_4Ni_2)_{100-y}X_y$ (X=O,N) Specimen

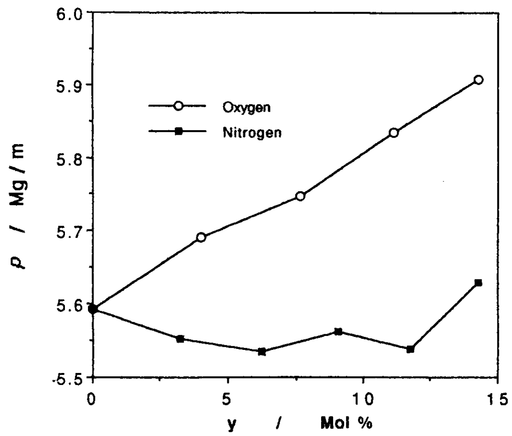


Fig. 7 Relation between Specific Gravity and Molar Fraction of Oxygen and Nitrogen in $(Ti_4Ni_2)_{100-y}X_y$ (X=O,N) Specimen

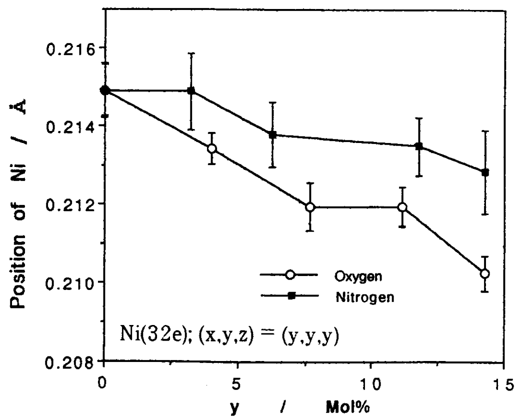


Fig. 6 (b) Relation between Nickel Position and Molar Fraction of Oxygen and Nitrogen in $(Ti_4Ni_2)_{100-y}X_y$ (X=O,N) Specimen

The resistivity gradient change in Ti_4Ni_2N could suggest that over 230 K its atomic vibrations increased much larger than that of the other specimens. Usually an increase of viscosity is caused by a decrease of free space or an increase of covalency in materials. Though the increase of oxygen causes the decrease of free space, it does not affect viscous property of the Ti_4Ni_2O phase. We imagine the covalency bonding effect of nitrogen with either titanium or nickel might cause the increase of viscosity through forming chain bondings between atoms. We have not gotten any certainty for the viscous property change.

5. Conclusion

The solubility and effects of interstitial elements (oxygen, nitrogen, and carbon) to the Ti_2Ni phase were studied. Though oxygen is soluble in the compound as much as 14 at%, the other light elements are not. The addition of nitrogen to the compound affects a rapid increase of viscosity and gradient change of resistivity. The reasons for these anomalies have not been cleared yet.

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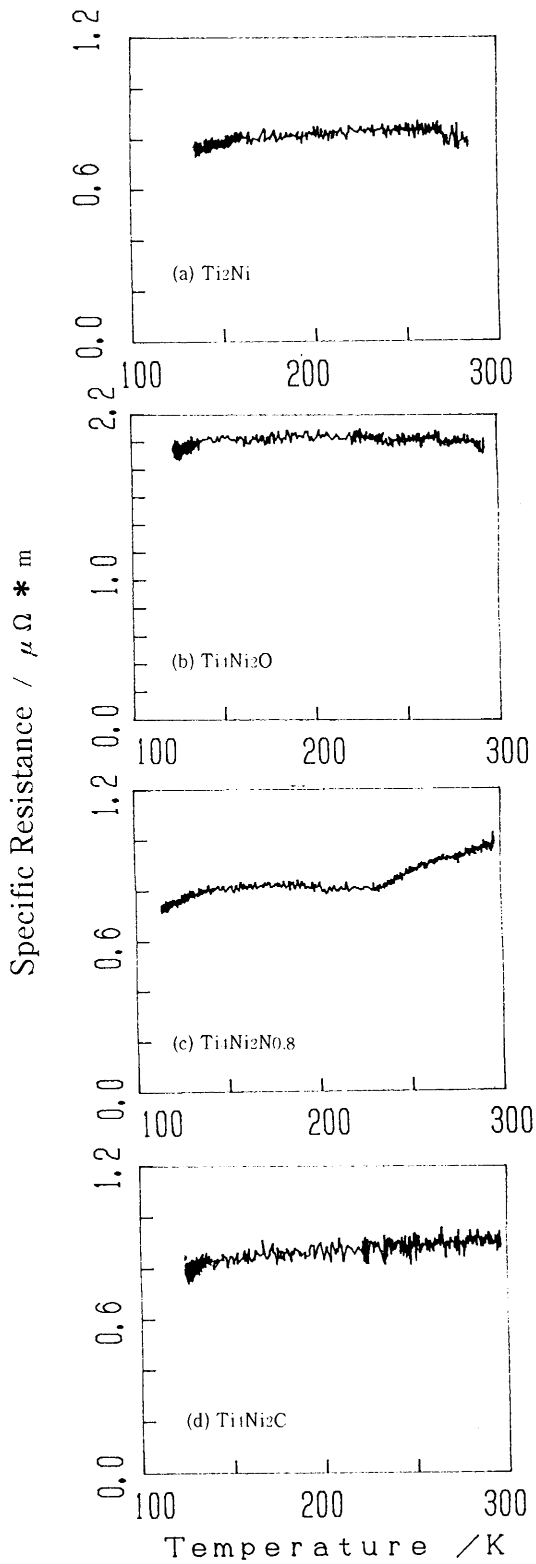

Fig. 8 Temperature dependance of specific resistance in (a) Ti_2Ni, (b) Ti_4Ni_2O, (c) Ti_4Ni_2N, (d) Ti_4Ni_2C