MECHANICAL PROPERTIES OF FeTi, CoTi, AND NiTi
AT ELEVATED TEMPERATURES

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Introduction

It is well known that intermetallic compounds are brittle at room temperatures but fail with sufficient plastic deformation above 0.5 Tm and that the strength of intermetallic compounds is relatively high because of these high elastic modulus. Since the strength of intermetallic compounds is essentially related to the bonding force and is not involved in the strengthening mechanisms such as martensitic transformation and precipitation, intermetallic compounds seem to be useful for the high temperature materials.

The compounds having CsCl structure are one of the groups of the intermetallic compound family which consist of huge number of compounds. About 200 of intermetallic compounds have been identified to have CsCl structure(1). It is clear from the phase diagrams determined that almost all the compounds having CsCl structure have homogeneity range at elevated temperatures(2)(3)(4).

The intermetallic compounds which have homogeneity range contain structure defects at non-stoichiometric compositions to achieve the required composition with ordered structure(5). According to a simple calculation, the concentration of the defects attains $1 \times 10^{-2}$ for substitutional atoms and $2 \times 10^{-2}$ for vacancies at the composition of 1 at% off from the stoichiometry. It is, therefore, obvious that the mechanical properties of non-stoichiometric compounds are largely affected by the defects.

This investigation was undertaken by means of compression test and hot hardness measurement in order to evaluate the effect of the structure defects on the strength of FeTi, CoTi, and NiTi. They have CsCl structure and have wide homogeneity range. The type of the structure defects introduced at non-stoichiometric compositions was already determined by density measurements and was confirmed to be substitutional wrong atoms at the Ti deficit side of the stoichiometry for each compounds(6).

Experimental

Samples were prepared by non-consumable arc melting under gettered argon using sponge titanium of ELI grade, electrolytic iron, electrolytic cobalt, and electrolytic nickel as starting materials. These elements were weighed and mixed to have 100 g of charge weight and then melted. Ingots were remelted more than three times to minimize segregation. All ingots obtained were weighed again to detect the weight loss during the melting. The specimens used in this investigation were prepared from the ingots which showed less than 0.1 % of weight loss. The ingots were annealed in dynamic vacuum for more than 25 hr at 1000°C to insure homogenization. The ingots were then canned in mild steel and forged on a conventional forging press at temperatures from 850 to 950°C. The specimens having 3 x 3 x 9 mm in size were cut by multi-wire saw from the forged plate which was taken out from the can. In order to normalize, all specimens were sealed in evacuated quartz ampoules and annealed for 1 hr at 1050 °C for FeTi and at 1000°C for CoTi and NiTi prior to further heat treatments.
All heat treatment were performed under vacuum of more than \(2 \times 10^{-5}\) mmHg. When rapid cooling is necessary the specimens were quenched by breaking the quartz ampoules under water. Hot hardness measurements were carried out by means of Vickers hardness tester which is equipped with evacuated specimen chamber in a load of 300 g. Compressive strength measurements were carried out on an Instron type testing machine at temperatures from R.T. to 900°C at a strain rate of \(9.3 \times 10^{-4}\) sec\(^{-1}\) installing evacuated chamber with tantalum heater.

Results

1. FeTi

The change in hardness of FeTi with temperature is shown in Fig. 1. The hardness of FeTi remains constant up to 300°C then decreases with increasing temperature. Hardness level of the non-stoichiometric compound is higher than that of stoichiometric compound. The relation between temperature and yield stress of FeTi is shown in Fig. 2. Though FeTi behaves in brittle manner below 500°C the compound is completely ductile above 600°C. Therefore, yield stress measurements could be performed without any difficulty above the temperature. The yield stress of FeTi decreases steeply with increasing temperature in the temperature range from 600 to 900°C. The yield stress of non-stoichiometric FeTi is higher than that of stoichiometric compound in the ductile fracture range.

2. CoTi

The change in hardness of CoTi with temperature is shown in Fig. 3. The hardness of non-stoichiometric CoTi decreases gradually with temperature up to 400°C and then decreases rapidly above the temperature. The hardness of CoTi having stoichiometric and near stoichiometric compositions remains constant up to 400°C. It is also clearly observed that the hardness of CoTi increases as the composition deviates from the stoichiometry. This tendency, however, becomes small at higher temperatures. The relation between temperature and yield stress of CoTi is shown in Fig. 4. CoTi compounds fail without plastic deformation below the specific temperature. However, above that temperature they show completely ductile behavior. The brittle to ductile transition temperature varies with deviating composition from the stoichiometry. The more the composition deviates from the stoichiometry the higher the transition temperature becomes. In the ductile fracture range yield stress of the compound decreases rapidly with increasing temperature.

3. NiTi

In this investigation, hardness and yield stress measurements for NiTi were carried out on the specimens which were quenched from 1000°C because NiTi phase has wide homogeneity range at high temperature but restricted around room temperature(2). Therefore, it should be minded that the data obtained below 600°C are irrelevant for discussing the effect of structure defects on the mechanical properties precisely.

The change in hardness of NiTi with temperature is shown in Fig. 5. The hardness of quenched NiTi keeps initial value up to 400°C and then decreases with increasing temperature. At room temperature, the hardness of NiTi increases as the composition deviates from the stoichiometry. However, only a little composition dependence was observed above 600°C. The relation between temperature and yield stress of NiTi is shown in Fig. 6. It is obvious that the plastic behavior of stoichiometric NiTi is completely different from the
Fig. 1 Temperature dependence of hardness of FeTi

Fig. 2 Temperature dependence of yield stress of FeTi
Fig. 3  Temperature dependence of Hardness of CoTi

Fig. 4  Temperature dependence of yield stress of CoTi
Fig. 5 Temperature dependence of hardness of NiTi

Fig. 6 Temperature dependence of yield stress of NiTi
non-stoichiometric compound. The stoichiometric NiTi is ductile at all temperatures tested and also shows anomalous behavior in the temperature range between R.T. and 400°C. Non-stoichiometric NiTi shows the same plastic behavior as was observed in FeTi and CoTi. In the NiTi, brittle to ductile transition was observed around 400°C. The relatively small composition dependence of yield stress was also observed.

Discussion

1. Temperature dependence of yield stress in stoichiometric NiTi

In the measurements of temperature dependence of yield stress, brittle to ductile transition was clearly observed around 0.5 Tm in FeTi, CoTi, and non-stoichiometric NiTi. Only the stoichiometric NiTi was ductile at all temperatures tested and showed to have anomalous temperature dependence of yield stress in the temperature range from R.T. to 200°C followed by temperature independent range between 200 and 400°C. The same behavior has been reported by Rozner and Wasilewski(7) in tensile testing. The cause of this anomalous behavior will be discussing fully now.

The temperature dependence of yield stress of intermetallic compounds having CsCl structure has been measured on AgMg(B) and NiAl(7). The general trend obtained is that the temperature dependence of yield stress is small at the temperatures below 0.5 Tm but large above that temperature and no anomaly exists. It is well known that in some intermetallic compounds which have Ll2 structure yield stress increases with increasing temperature at specific temperature range. In order to explain the anomaly, several theories have been proposed(9). But no successful explanation has been given.

In stoichiometric NiTi there are two distinguished phenomena affecting the plastic behavior around room temperatures. One is stress induced martensitic transformation and the other is elastic modulus anomaly which was first observed by Wasilewski(10). When the stress is applied at the temperatures between Mf and Md mother phase must transform into martensite. This causes stress relaxation at relatively low stress level and consequently yield like profile is observed in a stress-strain curve. However, Md temperature of stoichiometric NiTi was reported to be 130°C by Sastri and Marcinkowski(11). So that above 130°C the elastic modulus anomaly is considered to be a main factor affecting the yield stress. As a matter of fact, elastic modulus of stoichiometric NiTi increases with increasing temperature from Ms to 600°C, and as shown in Fig. 6, the yield stress changes with temperature in the same manner as the elastic modulus does. Therefore, it may be concluded that the yield stress anomaly observed in stoichiometric NiTi is caused by both stress induced martensitic transformation and the elastic modulus anomaly.

2. Effect of structure defects on hardness and yield stress

Fig. 7 illustrates the relation between hardness and composition for CoTi which has wide homogeneity range. It is clear from the figure that hardness minima appear at the stoichiometric composition throughout the temperatures tested, that the hardness increases as the composition deviates from the stoichiometry below 0.5 Tm, that above 0.5 Tm the increase in hardness with composition becomes small and that the hardness maxima appear at specific composition in the off stoichiometry. In other words, the introduction of structure defects is effective to increase the hardness below 0.5 Tm but the introduction of large amount of the defects causes the decrease in hardness for off-stoichiometric CoTi above 0.5 Tm. The same tendency has also been observed in several compounds having CsCl structure(12)(13)(14). In these compounds hardness maxima were clearly observed above 0.6 Tm. This behavior can be
Fig. 7 Hardness isotherms as a function of composition for CoTi

Fig. 8 Yield stress isotherms as a function of composition for CoTi
explained by the following idea that though structure defects act as barriers against the motion of dislocations at lower temperatures where deformation is controlled by slip, the defects even substitutional atoms act as preferred jump site at higher temperatures where the deformation is mainly controlled by diffusion. This idea is considered to be strongly supported by the fact that diffusion coefficient increases as the composition deviates from the stoichiometry in AgMg, AuCd, AuZn, Ni rich side of NiAl, Co rich side of CoAl, and Ni rich side of NiTi(16)(17)(18)(19)(20) where substitutional wrong atoms exist as structure defects(6)(21). Demian et al(19) theoretically gave the following concept by using the random walk theory and six jump mechanism that the activation energy of diffusion should decrease as the composition deviates from the stoichiometry. If the maximum of the activation energy of diffusion means the minimum of the diffusion coefficient this may be the strong evidence to support the fact that the diffusion coefficient of the compounds increases as the composition deviates from the stoichiometry.

In this investigation, the activation energies of diffusion for FeTi, CoTi, and NiTi were obtained from the relation between hardness and temperature, such as \( H = A \exp(2Q/RT) \), by using the procedure proposed by Sherby and Armstrong(22). However, no clear relation was obtained.

As shown in Fig. 8, the introduction of substitutional atoms brings increase in yield stress at relatively lower temperatures of the ductile fracture range but little increase in yield stress was given at higher temperatures. This behavior is completely identical with the hardness does and may be attributed to the action of substitutional atoms. In fact, the same tendency has been obtained in the measurements of flow stress of AgMg. It also has CsCl structure(10). In the AgMg, it was found that the introduction of structure defects causes the decrease in flow stress at temperatures near \( T_m \).

**Conclusion**

In order to clarify the effect of structure defects on the mechanical properties of FeTi, CoTi, and NiTi which have CsCl structure and wide homogeneity range, the change in hardness and yield stress with temperature were measured.

Stoichiometric NiTi showed sufficient ductility at all temperatures tested. However, the relation between yield stress and temperature is rather complicated. The NiTi showed yield stress anomaly between R.T. and 200°C where yield stress increases with increasing temperature. The cause of the anomalous behavior is considered to be due to both stress induced martensitic transformation and elastic anomaly.

The effect of structure defects on yield stress and hardness was clearly observed in CoTi because CoTi has relatively wide homogeneity range. The hardness is largely affected by the structure defects at lower temperatures. However, the effect becomes small as temperature increases. The hardness maxima were observed above 0.6 \( T_m \). In yield stress measurements, brittle to ductile transition was observed around 0.5 \( T_m \). The transition temperature increases as the composition deviates from the stoichiometry. The relation between yield stress and composition in the ductile fracture range is almost the same as in hardness.

The decrease in hardness and yield stress with increasing amount of structure defects observed at the compositions where large amount of structure defects exist can be explained by the fact that in the intermetallic compounds having CsCl structure, diffusion coefficient increases as not only vacancies are introduced but also substitutional atoms are introduced. Therefore, stoichiometric compounds should be chosen for high temperature materials.
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References