Formation of Nonequilibrium Phases at Collision Interface in an Explosively Welded Ti/Ni Clad

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Microstructural modifications of collision interface in an explosively welded Ti/Ni clad were studied by transmission electron microscopy. Nonequilibrium phases such as amorphous and icosahedral quasicrystalline phases were synthesized and locked into the collision interface. These products were concluded to be the trace of melting and subsequently rapid solidification of thin layers along the contact surface of both the parent materials. It was considered that the impact pressure during explosive welding promoted the formation of the nonequilibrium phases. The solidification process of the molten layer was also discussed.

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I. Introduction

Nonequilibrium phases, i.e., amorphous, quasicrystal and supersaturated solid solution, have been extensively studied by means of rapid solidification and mechanical alloying. In the material processing using shock energy such as explosive welding and powder compaction, a significant high pressure and temperature increment is induced within a few microseconds⁽¹⁾⁻⁽³⁾. Severe plastic deformation, extensive mechanical mixing, surface cleaning and exposure of fresh surfaces occur under these conditions. Recently, shock-wave synthesis of intermetallic compounds has been carried out using elemental metal powder mixtures⁽⁴⁾⁻⁽⁶⁾. On the other hand, we have reported that the amorphous phases and the supersaturated solid solution of β -Ti phases were formed at the bonding interface in the explosively welded Ti/austenitic stainless and low carbon steels clads⁽⁷⁾. It was concluded that the melting layer is responsible for the bonding of explosively welded Ti/steel clads. These results indicate that the shock processing of materials has the combined characteristics of rapid solidification, mechanical alloying and combustion synthesis. Thus, it is likely that the shock processing of materials can create new nonequilibrium phases.

The purpose of the present study is to elucidate the synthesis of such nonequilibrium phases as amorphous and quasicrystalline phases at the collision interface in the explosively welded Ti/Ni clad material.

II. Experimental Procedures

Commercially pure grade titanium (99.8 mass%, provided by Nippon Steel Corporation, Hikari 743, Japan) and nickel (99.7 mass%, purchased from The Japan Lamp Industries Co., Ltd., Chuou, Tokyo 104, Japan) were used in the present study. Before cladding, plates of both materials $90 \times 40 \times 5$ mm³ in size were annealed at 973 K for 5.4 ks in a vacuum of 2×10^{-3} Pa. They were mechanically ground to remove the oxide scale, subsequently polished with emery papers and finally rinsed in acetone with ultrasonic cleaner. A preset angle stand-off configuration⁽⁸⁾ was used for the present explosive experiments as shown in Fig. 1. The preset angle was 7°. The explosive used was plastic explosive (SEP, provided by Asahi Chemical Industry Co., Ltd., Chiyoda, Tokyo 100, Japan) consisting mainly of nitric ester. The detonation velocity of the explosive was about 6900 m/s. The flyer plate was titanium. The flyer plate velocities were varied from 320 to 1150 m/s. The opti-

Fig. 1 Schematic illustration of experimental assembly for explosive welding.

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imum velocity to complete the intimate contact was about 470 m/s which was determined by preliminary experiment. The corresponding collision pressure is estimated to be 5.2 GPa⁽⁸⁾. After explosive welding, the specimens for scanning electron microscopy (SEM) were cut parallel to the detonation direction. They were mechanically polished with emery paper and then finished with aluminum powders. Specimens for TEM observations were prepared from slices which were cut parallel to the detonation direction, and mechanically ground to thickness of about 0.15 mm. Disks of 3 mm in diameter containing the collision interface were spark-cut and electropolished using the twin jet method in an electrolyte consisting of 20% sulfuric acid and 80% methanol in volume. They were finished with an argon ion beam milling machine. Selected area and micro-diffraction experiments, TEM observations and microanalyses were carried out in a JEOL-2000FX microscope operated at 200 kV and equipped with a ± 45 degrees double tilt holder and a Tracor Northern energy dispersive X-ray (EDX) micro-analytical system. A standardless EDX technique was used to estimate EDX spectra. The beam size in the micro-diffraction experiments and the microanalyses was about 40 nm or less in diameter.

III. Results and Discussions

Figure 2 shows SEM micrographs of the collision interface in the explosively welded Ti/Ni system. The interface has somewhat irregularly wavy shape as shown in Fig. 2(a). Figures 2(b) and (c) are the enlarged SEM micrographs corresponding to the waves B and C in Fig. 2(a). There are two distinct features as indicated by the single and double arrows in Figs. 2(b) and (c). The former is the interface at which Ti and Ni are directly connected. The latter is the so-called vortex zone within the Ni plate, where Ti and Ni are considered to be mechanically mixed and melted during the explosive welding since polycrystalline TiNi intermetallic compounds with B2 structure were observed by TEM. The TiNi phase consisted of irregular grains of 500 nm in average diameter. This phenomenon is the evidence of a kind of shock synthesis. However, the explanation is not further described here since it is irrelevant to the purpose of the present study.

More interesting phenomena were observed in the former region. Figure 3(a) shows a bright field image of the collision interface between Ti and Ni parent materials. Ti is the upper side and Ni is the lower side in the micrograph. This sequence is constant throughout the present paper. One can clearly see the interface in the center part of the micrograph. Diffuse halo ring and ring pattern consisting of diffraction spots were seen in a selected area diffraction pattern taken from the whole interface. This indicates that the interface is composed of amorphous and fine crystalline phases. There are three regions as marked with I to III at the interface. To obtain further information on the constitution phases of the interface, micro-diffraction experiments were carried out. Figure 3(b-1) is a micro-diffraction pattern taken from the columnar grain B in the region I in Fig. 3(a). The pattern shows the fivefold symmetry. The threefold and twofold symmetry patterns are also obtained from the other grains in the same area as shown in Figs. 3(b-2) and (b-3), respectively. It is apparent that an icosahedral quasicrystalline phase⁽⁹⁾ (*i*-phase) forms at the region I in the collision interface. Figure 3(c) shows a micro-diffraction pattern taken from the particle C in the region II in Fig. 3(a), which corresponds to the [123] zone axis of fcc structure with $a_0 = 1.13$ nm. All the patterns taken from similar

Fig. 2 (a) SEM micrographs showing wavy collision interface in the explosively welded Ti/Ni clad. (b) and (c) Enlarged SEM micrographs of waves B and C in (a), respectively.

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Fig. 3 (a) Bright field image showing synthesized products at collision interface in explosively welded Ti/Ni clad. (b-1) to (b-3) Micro-diffraction patterns taken from the several grains of the region I in (a), showing five, three and two-fold symmetries of *i*-phase, respectively. (c) to (e) Micro-diffraction patterns taken from the areas C to E in (a), respectively.

particles were consistently indexed by the above lattice parameters. Therefore, the particles in the region II are determined to be $\text{Ti}_2\text{Ni}^{(10)-(11)}$ intermetallic compound. On the other hand, a pattern taken from the area D in the region II consists of a broad halo ring as shown in Fig. 3(d), indicating the formation of an amorphous phase in the area D. Figure 3(e) shows a micro-diffraction pattern taken from the particle E in the region III in Fig. 3(a), which corresponds to the [001] zone axis of B2 structure with $a_0 = 0.31$ nm. The particles in the region III are considered to be a high temperature phase of TiNi intermetallic compound with B2 structure⁽¹⁰⁾⁽¹²⁾.

Figure 4(a) also shows a bright field image of another collision interface between Ti and Ni parent materials. The constitution of the interface is different from that in

Fig. 3(a). There are four regions as marked with I to IV in the interface. Figures 4(b) to (e) are micro-diffraction patterns taken from the areas B to E in the regions I to IV in Fig. 4(a), respectively. The patterns in Figs. 4(b) and (d) show the identical fivefold symmetry as in Fig. 3(b-1). The same threefold and twofold symmetry patterns as in Figs. 3(b-2) and (b-3) were also recorded from several grains in the regions I and III. It can be concluded that the regions I and III consist of the *i*-phase. Since crystalline contrast was absent during tilting experiment, an amorphous phase is considered to be dominant in the region II. However, there are fine particles about 20 nm in diameter as indicated by the single arrows in the amorphous phase. It is notable that the ratio of the diameter between the second and first rings is about 1.6 in the

Fig. 4 (a) Bright field image showing synthesized products at collision interface in explosively welded Ti/Ni clad. (b) to (e) Micro-diffraction patterns taken from the areas B to E in (a), respectively. (f) Enlarged bright field image of the region I in (a). (g) Dark field image of the region III in (a) taken by using a diffraction spot G in (d).

diffraction pattern in Fig. 4(c). This fact suggests that quasicrystalline particles are dispersed in the amorphous matrix. Figure 4(e) shows a micro-diffraction pattern taken from the region IV. The pattern can be indexed as the [011] zone axis of B2 structure with $a_0 = 0.31$ nm. The product adjacent to the Ni parent material is the high temperature phase of TiNi intermetallic compound the same as that in Fig. 3. However, the grain size of TiNi phase in Figs. 3(a) and 4(a) is quite different, i.e., that in the former is about 25 nm in average diameter and that in the latter is more than 600 nm in longitudinal direction at least as shown in Fig. 4(g). This may be related to the difference of cooling rate. No Ti_2Ni intermetallic compound was observed in this case. This reason is not clear now. Figure 4(f) shows the enlarged bright field image of

the region I in Fig. 4(a). The quasicrystalline grains have rectangular or square shape. The average size of those is about 100 to 150 nm in one-side. It was confirmed that each grain has random orientation by diffraction experiments. There is dendritic structure in the grains. The dendrite arms spread from the Ti side to the amorphous phase in the region II. This indicates that the quasicrystalline phase nucleates heterogeneously and grows from the contact surface between Ti and the molten layer. On the other hand, the quasicrystalline grains in the region III have a square shape about 50 nm on the one-side and the cellular solidification fronts of them are observed toward the amorphous phase in the region II as indicated by the double arrows in Fig. 4(a). Figure 4(g) shows the dark field image of the region III taken by using a diffraction

spot G in Fig. 4(d). The wide range of the region III is in contrast in the dark field image. In other words, the quasicrystalline grains in the region III are preferentially oriented. The solidification temperature of the TiNi compound⁽¹⁰⁾ in the region IV is considered to be the highest among the synthesized products in the present case. Therefore, the quasicrystalline phase in the region III might nucleate heterogeneously and grow from the primarily solidified TiNi compound in the region IV. These results suggest that there is a sort of orientation relationship between the quasicrystalline phase in the region III and the TiNi compound. This is now under study and will be reported in due course. The solidification sequence is presumed as follows from the above observations. The molten layer formed during explosive welding is firstly solidified as TiNi compound from Ni parent material side since the thermal conductivity of Ni is about 5 times higher than that of Ti⁽¹³⁾ and the solidification temperature of the TiNi compound is the highest among the synthesized products in the present case as mentioned above. Subsequently, the quasicrystalline phase in the region I is solidified from the contact surface between Ti and molten layer. At the same time the quasicrystalline phase in the region III is also formed from the contact surface between TiNi compound and molten layer. Consequently, the most undercooled part of molten layer is locked into as the amorphous phase in the region II. This solidification sequence is considered to be essentially the same as that in the collision interface presented in Fig. 3, although the structure and size of synthesized products are somewhat different.

In order to clarify the compositional dependence of the synthesized products, EDX analyses were carried out at the collision interface presented in Figs. 3 and 4. However, the results were inconsistent since the specimen surface was contaminated by the constituent elements of the parent materials during ion milling. For instance, Ni element more than 6 at% was detected in the Ti parent material far from the interface. In the same way, the surface of the Ni parent material was contaminated by Ti element. In addition, Al element about 15 at% which might be derived from the specimen holder of the ion milling used was counted from the whole area. The specimen prepared without ion milling is required for quantitative analysis.

Another example of nonequilibrium phase and intermetallic compound formations at the collision interface is presented in Fig. 5 (a). Figures 5(b) to (e) are micro-diffraction patterns taken from the areas B to E in Fig. 5(a). An amorphous phase is formed at the whole collision interface as clearly recognized from Figs. 5(b) and (c). There are crystalline particles D and E in the amorphous phase. The particle D is identified as Ti₂Ni compound by the corresponding diffraction pattern in Fig. 5(d). The pattern can be indexed as [112] zone axis of fcc structure with $a_0=1.13$ nm as mentioned above. The diffraction pattern in Fig. 5(e) can be indexed as the superimposed pattern of [1 $\bar{1}$ 0] zone axis of monoclinic structure with $a=0.2889$ nm, $b=0.412$ nm, $c=0.4622$

nm and $\beta=96.8^\circ$ ⁽¹⁰⁾⁽¹⁴⁾. This structure corresponds to the low temperature (martensitic) phase of TiNi intermetallic compound, which is well-known as the origin of shape memory effect. The pattern is in mirror symmetry with respect to the (001) plane. This indicates that there are (001) compound twins⁽¹⁵⁾⁽¹⁶⁾ as an internal defect of the martensitic phase in the particle E. Although we do not reproduce an enlarged micrograph, fine striations corresponding to the (001) twins were observed in the particle E. It is likely that the maximum temperature reached during the explosive welding and/or the cooling rate after the explosive welding in the present case are higher than those in the former two cases. The microstructural modifications at the collision interface in the explosively welded Ti/Ni clad are divided into three categories as presented in Figs. 3 to 5 and the nonequilibrium phases

Fig. 5 (a) Another example of bright field image of collision interface in explosively welded Ti/Ni clad, showing the formation of amorphous and crystalline phases. (b) to (e) Micro-diffraction patterns taken from the areas B to E in (a), respectively.

are synthesized in the all cases.

It has been reported by Aoki *et al.*⁽¹⁷⁾ that three kinds of nonequilibrium phases, i.e., amorphous, quasicrystalline and unidentified nonequilibrium crystalline phases were formed in the binary Ti-Ni system by melt-spinning. The fully amorphous phase was formed in the composition range of 30 to 45 at.% Ni. The amorphous phase was also observed partly with the crystalline phase such as TiNi intermetallic compound around the stoichiometric composition. The unidentified crystalline phase which transformed to the stable TiNi₃ phase at about 900 K was formed in the composition range of 67 to 75 at.% Ni. The unidentified and TiNi₃ phases were not detected throughout the present explosive experiment and the TiNi phase was observed near the Ni parent material as mentioned above. They also reported that the quasicrystal phase was distributed as fine particles with the average size between 1 to 10 nm in diameter in amorphous matrix of Ti-rich composition in the melt-spun specimen. Zhang *et al.*⁽¹⁸⁾ have also found the *i*-phase as small nodules of about 0.1 to 0.3 μm in diameter either in the amorphous matrix or together with the stable Ti₂Ni phase in rapidly solidified (Ti_{1-x}V_x)₂Ni alloys with $x=0.0$ to 0.3. Since the amorphous and quasicrystalline phases are formed between the Ti parent material and the Ti₂Ni or TiNi phases in the present study, both the nonequilibrium phases may also have Ti-rich composition. It is noteworthy that the *i*-phase observed in the present study occupies fairly large area of the collision interface, particularly at the interface in Fig. 4. This fact suggests that the impact pressure promotes the formation of the nonequilibrium phases. Sekhar *et al.*⁽¹⁹⁾⁽²⁰⁾ have reported that the rapid pressurization technique of liquid metals has been shown both theoretically and experimentally to yield appreciable undercooling. Since the rapid pressurization conducts the rising of liquidus temperature, the adiabatic heat release and the improvement of the thermal contact at the liquid metal/die interface, the resultant undercooling is increased. Sekhar and Rajasekharan⁽²¹⁾ have demonstrated experimentally that the undercooling resulting from rapid pressurization can promote the formation of nonequilibrium phases in the Al₈₀Mn₂₀ alloy. The present explosive welding process is considered to be a sort of rapid pressurization technique.

In conclusion, nonequilibrium phases such as amorphous and icosahedral quasicrystal, and intermetallic compound phases were synthesized and locked into the collision interface in the explosively welded Ti/Ni clad. These products were considered to be the trace of melting and subsequently rapid solidification of thin layers along the contact surface of both the parent materials. The microstructural characterization of the collision interface in the explosively welded clad will supply the important information on the formation ability of nonequilibrium phases in binary alloy systems. The effect of impact pres-

sure on the formation ability of nonequilibrium phases will be estimated by the further quantitative analyses. In addition, this technique will be extended to not only the other binary but also multicomponent systems by selecting appropriate alloy compositions and systems as the cladding materials.

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