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Correlation of Cold Work, Annealing, and Microstructure in Zircaloy-4 Cladding Material

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지르칼로이-4피복재에서 가공도, 열처리 및 미세조직과의 상호관계

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Abstract

To obtain various necessary data for the manufacturing and the use of the nuclear fuel cladding tube, the effects of deformation and heat treatment on Properties of Zircaloy-4 material have been studied. The hardness is increased rapidly at a low degree of cold work and increased gradually at cold work above 10%. Recrystallization has been completed at 640°C, 590°C, and 555°C in 30 %, 60% and 80% cold worked specimen, respectively. The transformation of microstructure with increasing cooling rate after β-annealing is as follows; coarse Widmanstatten(α) →fine parallel plate(α) →martensite(α'). At the same time, hardness increased with increasing cooling rate.

요 약

핵연료 피복관 제조 및 사용시에 필요한 자료를 얻기위하여 지르칼로이-4재료에서 가공과 열처리의 영향을 조사하였다. 지르칼로이-4 재료는 저가공도에서는 경도가 급격히 증가하지만 10% 이상 가공도에서는 점진적으로 증가하였다. 냉간가공된재료의 재결정은 가공도가 30%, 60%, 80%로 증가함에 따라서 640°C, 590°C, 555°C에서 각각 완료되었다. β구역에서 열처리한후에 노냉, 공냉, 수냉을 하였을 때 냉각속도가 증가함에 따라서 경도는 증가하고, 조직은 coarse widmanstatten(α)→fine parallel plate(α)→martensite(α')순으로 변화한다.

1. Introduction

Zircaloy-4 material has been used as the fuel cladding materal in the nuclear power plants because of its good mechanical strength and ductility and low thermal neutron absorption cross section. Cladding tube has been imported to date however a study for localization has recently been undertaken.

Basic metallurgical properties of Zircaloy-4 must be studied to obtain proper manufacturing technology for good material performance. The one of the important factors influencing tube properties is microstructure which is controlled by annealing and deformation. Microstructure is controlled to have α phase with fine grain size for good ductility in the commercial manufacturing process.[1~4] Good mechanical properties are obtained by the careful control of cold reduction and annealing in the final stage of the manufacturing processes.[5] The most important process in the total manufacturing processes is the cold reduction and annealing process which is affected by various factors. Therefore, the work-hardening and recrystallization behaviors of Zircaloy-4 material have been examined in this study to obtain useful data for annealing time and temperature in the tube manufacturing process for localization and safety analysis. β-quenching is one of important processes for advanced fuel cladding materials in recent years. Therefore, this phase transformation characteristic of the material have been also studied by controlling the cooling rate after annealing in β phase.

2. Experiment

The material used in this study is Zircaloy-4 plate manufactured commercially and specimens have been cold rolled by 10%, 20%, 30%, 40%, 50%, 60%, 70%, and 80% at room temperature. Rolling has been carried out through many passes at a reduction rate of about 2% per one pass. The hardness has been measured by a Knoop hardness tester on the transverse plan to the rolling direction due to anisotropy of the hardness.[6] The value of hardness has been taken value obtained from the data measured more than ten times on the same specimen. The heat treatment has been performed in a vacuum of 10^{-4} torr and all specimens have been annealed at vaious temperatures ranging from 300°C to 800°C for 1 hour in a furnace having uniform temperature region. For optical microscopy, the samples have been ground to Grid 600 of abrasive paper, polished to 0.05m of alumina powder, and then were etched in a solution of nitric acid, water, and hydrofluoric acid at a ratio of 45:45:10. And then microstructures have been observed with a polarized microscope. Grain sizes have been measured repeatedly five times with the same specimen by the linear intercept method. To study the effect of cooling rate on the microsturcture, specimens have been annealed at 1050°C for 30 minutes and have been cooled in the furnace, air, and water.

3. Result and Discussion

3.1. Work hardening of Zircaloy-4

Fig. 1 shows the variation of hardness with increasing the degree of cold work. The hardness has been rapidly increased up to Knoop hardness 200 at a low degree of cold work (about 10%) and gradually increased at a cold work more than about 10%. Fully annealed materials show such a behavior. It can be explained that rapid work hardening occurs in this material at a low cold work by internal defects such as dislocations and other defects which were introduced by deformation. However, the amount of

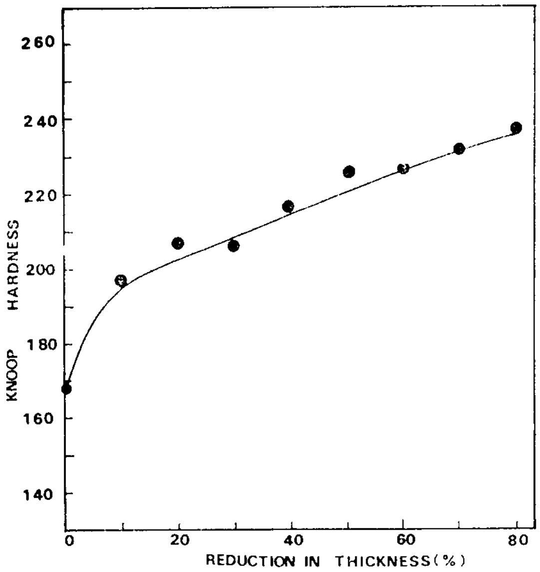

Fig. 1. Relation Between Hardness and Deformation Degree for Zircaloy-4

hardness-change is decreased by the same amount of additional cold work as the total cold work is increased since materials already contained many defects in the low cold work.

Zircaloy has HCP structure in α-region. And a possible deformation mode is slip in case stress is applied vertically to the basal pole and is twin in case stress is applied parallelly to the basal pole. This material has a good strength when it has its basal pole to parallel with the stress direction in the most of grains because flow stress for slip deformation is lower than that for twin deformation.[7] The Commercial Zircaloy cladding tubes are produced to have the basal oriented to the radial direction and it can be expected to have good strength radially.

3. 2. Recrystallization behavior

Recrystallization behavior can divided be into recovery, recrystallization, and grain growth.

Fig. 2 shows the recrystallization behavior of Zircaloy-4 material. Cold worked Zircaloy-4 retains its initial hardness up to a certain temperature above which softening occurs quite abruptly. The hardness decreased rapidly at temperatures between 500°C and 600°C and was almost constant at temperatures above 600°C. Although the starting temperature of recrystallization could not be measured precisely, it is observed from Fig. 2 that the recrystallization starts within a range of temperature between 500°C and 520°C. And recrystallization occurs quickly and the temperature range showing recrystallization become narrower as cold work increases. Fig. 3 shows that the recrystallization has been completed at about a temperature of 640°C, 590°C and 555°C at a cold work of 30%, 60%, and 80%, respectively. The stored energy in material increases as cold work increases and the critial nucleus size and activation energy for recrystallization decrease with the increase of stored energy.[8,9] Also, the moving rate of interface increases with the increase of stored energy. Therefore, recrystallization temperature decreases because nucleation and growth of grains become easy as the cold work increases.

Fig. 4 shows a relationship between grain size and cold work after annealing at 700°C

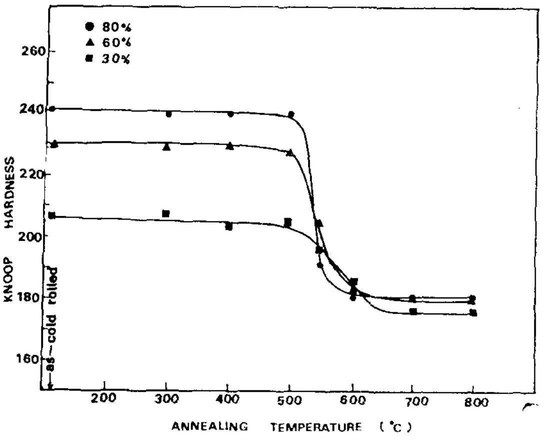

Fig. 2. Variation of Hardness of the Cold-Rolled Zircaloy-4 with Annealing Temperature
(Annealing time: 1 hour)

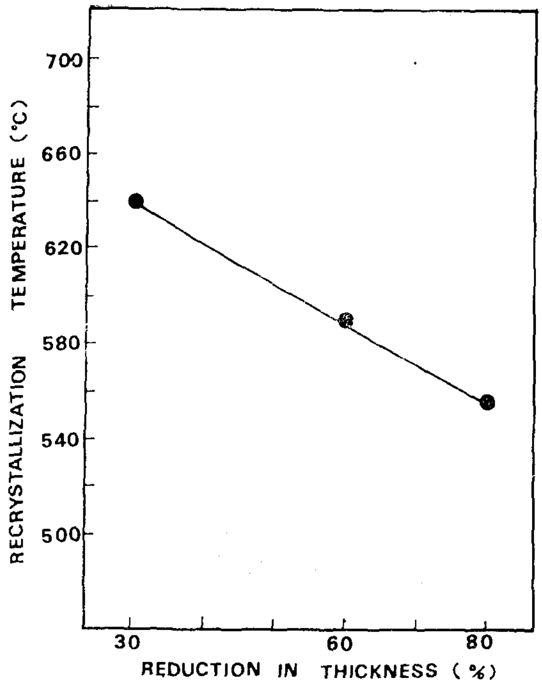

Fig. 3. Relation Between Recrystallization Temperature and Deformation Degree for Zircaloy-4

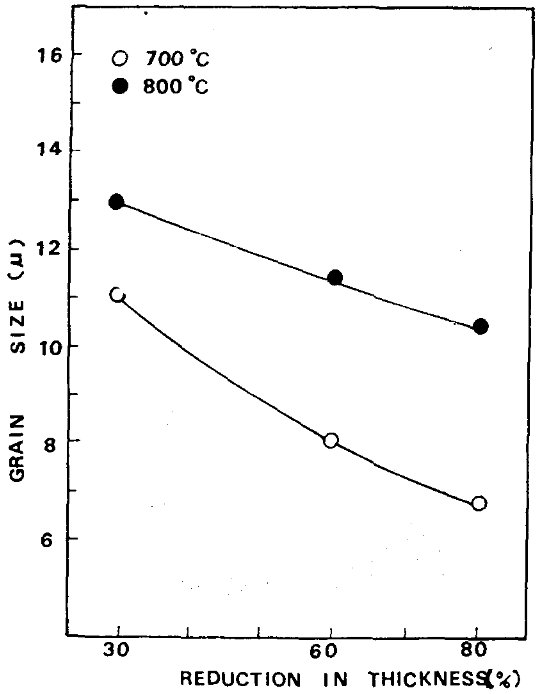

***Fig. 4.* Relation Between Grain Size after Recrystallization and Deformation Degree.**

and 800°C at which recrystallization is almost completed. Grain size after recrystallization decreases as cold work increases and grain growth in the high cold worked specimens occurs more rapidly than that in the low cold worked.

Fig. 5 shows microstructures with recrystallization behavior. Grain boundaries could be distinguished in the case of 30% cold work, but they could not be distinguished in the case of 60% and 80% cold work since the grains were elongated too much. After annealing at 550°C for 1 hour, recrystallization began partially in 30% cold worked material and occurred as much as a half of that in 60% cold worked material. And the grains of 80% cold worked material have been replaced with new grains because recrystallization was completed. Microstructures at above 550°C show the grain growth of recrystallized grain.

3-3. The beta to alpha phase transformation

Fig. 6 shows microstructures with cooling rate after annealing at 1050°C for 30 for 30 minutes

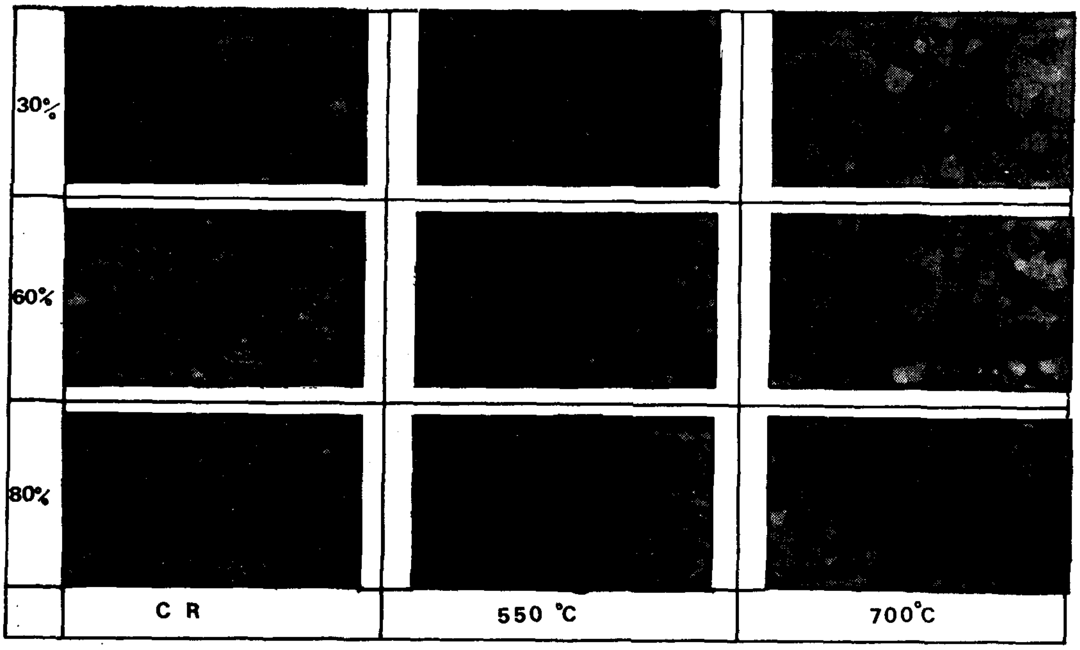

Fig. 5. Microstructures of the Zircaloy-4 with Heating Temperature with respect to Deformation Degree (Annealing time: 1 hour)

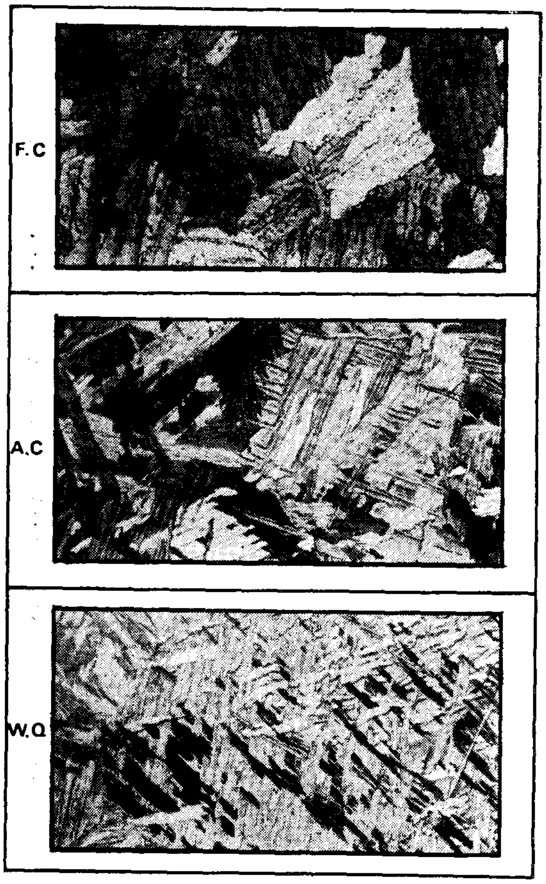

Fig. 6. Variation of Microstructures of the β-Annealed Zircaloy-4 with Cooling Rate

in Zircaloy-4 material. In the case of furnace cooling, the microstructure is coarse Widmanstatten(α) that consists of non-parallel structure resulting from random formation of plates in one grain and precipitations are observed at the boundary or in the matrix of the plates. It is understood that precipitations are zirconium carbide of NaCl structure and second phase complicated in combination with carbons, silicons, and phosphors of low solubility.^{10,11} In the case of air cooling, the microstructure is fine parallel plate(α) that is formed on one habit plane of prior β grain and the plate width of which is narrower than that formed by furnace cooling is. In the case of water quenching, the microstructure is martensite($\acute{\alpha}$) that consists of needle-like structures similar to the martensite structure of ferrous materials in appearance and formation mode. From the microstructural observation, the sequence of structural formation with increasing cooling rate is as follows; coarse Widmanstatten(α) $\rightarrow$ fine parallel plate(α) $\rightarrow$ Martensite($\acute{\alpha}$). According to Woo$^{12,13)}$ the orientation relationship between the rusulting phase(α) and the mother phase(β) is known to be an exact or close to Burgers relation of phase transformation; $(110)_\beta // (0001)_\alpha$, $[111]_\beta // [1120]_\alpha$.

Fig. 7 shows the variation of the hardness with cooling rate for Zircaloy-4 materials. Generally, phase boundary consists of dislocations of low density and precipitations. And phase matrix contains subgrains and dislocation networks of low angle boundary. However, in the case of martensite structure, boundary consists of dislocations with high density and precipitations and matrix contains many tangled dislocations. Therefore, the number of dislocations increases with increasing the cooling rate and the hardness of the material increases as the results. Generally, β-quenching of Zircaloy-4 material in-

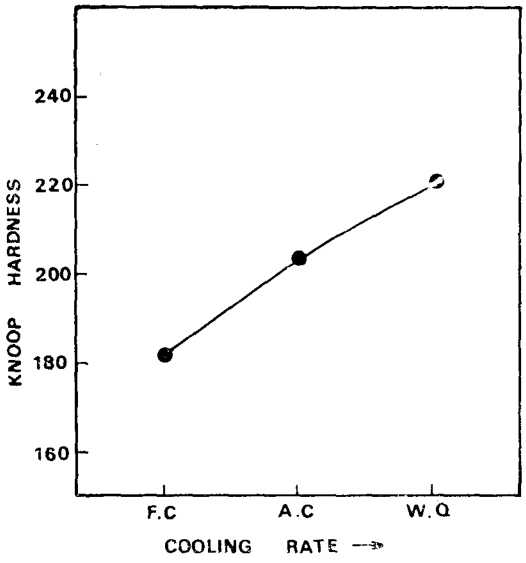

Fig. 7. Variation of Hardness of the β-Annealed zircaloy-4 with Cooling Rate

creases the yield strength and the corrosion resistance much without degrading the fatigue property and weldability.

4. Conclusion

1) The hardness increases rapidly in the case of low cold work(about 10%) and gradually with amost constant slope in the case of cold work above this value in this test range.
2) Recrystallization has been completed at a tempemperature of 640°C 590°C, and 555°C in 30%, 60%, and 80% cold worked specimen, respectively.
3) The Transformation of microstructures with cooling rate is as follows; coarse Widmanstatten(α)—fine parallel plate(α)—Martensite (α). At the same time, hardness increases by 40 Knoop hardness with as increasing cooling rate from furnace cooling to water quenching.

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