Atomic Energy of Canada Limited

PROSPECTS FOR ZIRCONIUM STRUCTURAL ALLOYS AT HIGH TEMPERATURES

by

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Paper 69-CNA-539 presented at the
1969 Canadian Nuclear Association Annual Conference
Montreal, June 8-12, 1969

Chalk River, Ontario

May 1969

AECL-3362

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ABSTRACT

Improved station efficiencies and lower capital costs provide incentives for the development of zirconium alloys for pressure tubes which can operate at temperatures above 450°C. The experience of the Ti industry indicates that a complex alloy containing solution hardeners of Sn or Al and precipitation hardeners of Mo and Nb and perhaps Si will be required. The thermal neutron cross-section of the alloy will be about 10% higher than Zircaloy-2 and because of its poor corrosion resistance will require cladding with a corrosion resistant alloy such as Zr-Cr. Results to date indicate that such a pressure tube is feasible.

PRÉCIS

Un meilleur rendement des centrales nucléaires et un coût moins élevé encouragent le développement d'alliages de zirconium pour les tubes de forces fonctionnant à des températures au-dessus de 450°C. L'expérience de l'industrie du Ti indique qu'un alliage complexe contenant comme durcisseurs des solutions de Sn ouAl ou des precipitations de Mo et Nb et peut être de Si serait necessaire. La section efficace pour les neutrons thermiques, de cet alliage sera environ de 10% plus élevée que pour le Zircaloy-2 et à cause de sa faible résistance à la corrosion devra être gainé avec un alliage résistant à la corrosion tel que le Zr-Cr. Les résultats jusqu'à présent indiquent qu'un tel tube de force est réalisable.

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INTRODUCTION

In the Canadian type of reactor which features heavy water moderation, natural uranium fuel and pressure tubes, there is a demand for low capture cross-section materials for structural components in the core. Zirconium alloys have filled this requirement so far because they are able to combine the properties of low neutron capture cross-section, high strength and high corrosion resistance in hot water.

The proven zirconium alloys, Zircaloy and Zr-2.5% Nb, give reasonable working stresses at the operating temperatures of reactors now built or under construction. Figure 1 shows maximum permissible working stress for these alloys as a function of temperature(1). The creep strength diminishes rapidly with temperature and above about 370°C becomes the criterion for selecting a design stress.

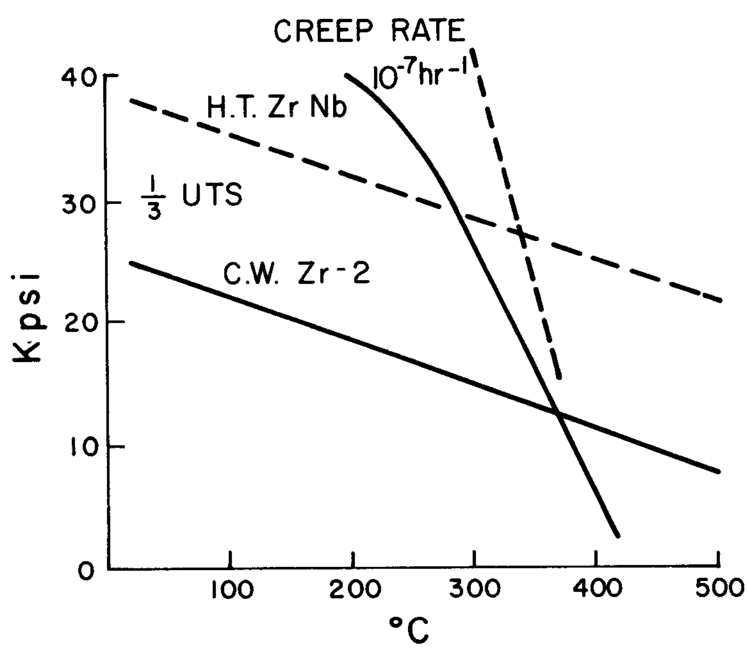


Figure 1 Design Stresses For Zr Alloys

To improve the efficiency and hence the capital cost, of CANDU reactors, the temperature of the outlet coolant must be raised significantly to temperatures above 450°C. The materials which have been developed to date for superheat are all high nickel alloys. These alloys are unsuitable for CANDU reactors because of their high neutron capture cross-section. We have examined the prospects of zirconium alloys for operation at temperatures near 450°C and find the results to be quite promising.

Most of the high strength zirconium alloys have poor corrosion resistance and it would be necessary to clad with a corrosion resistant alloy. Although this would make a production process complex, the complexity would have to be balanced against the rewards of higher efficiency.

OBJECTIVES

Our objective is to produce a pressure tube from a zirconium alloy which would have the following properties at a temperature of at least 450°C.

(a) a minimum stress of 34 to 45 kpsi as one-third of the ultimate tensile strength,

(b) a maximum creep rate of 10^{-7} h^{-1} after 5000 h at a stress of 10 to 12 kpsi,

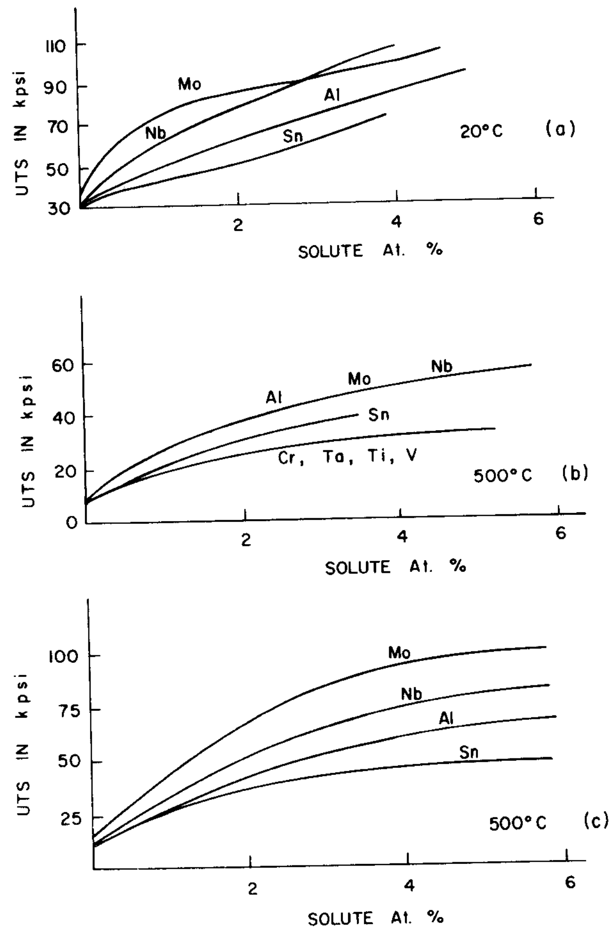
(c) a minimum of 25 kpsi as the stress to rupture in 100,000 h,

(d) a neutron capture cross-section of not more than 10% more than Zircaloy-2.

The corrosion behaviour of the alloy is not a limitation because techniques have been developed(2) for cladding it in a corrosion resistant alloy.

AVAILABLE INFORMATION ON HIGH STRENGTH ZIRCONIUM ALLOYS

From 1950 to 1960 extensive work was done in the U.S.A. and Russia to determine the effects of alloying additions of Al, Nb, Sn, Mo, Ti, Ta, Cr, Fe and V on the properties of zirconium. To achieve high strength at 500°C the most effective additions were the α-stabilizers, Al and Sn and the β-stabilizers Mo and Nb. Al and Sn are reasonably soluble in zirconium compared with other alloying elements and provide solution strengthening up to about 850°C. Mn and Nb have limited solubility in zirconium and their strengthening effect is due to the fine dispersion of precipitate which can be achieved by a quenching and aging treatment. Figure 2 shows the strengthening effect of these alloying additions in dilute binary alloys in the annealed condition, Figure 2(a) and (b) and in the β-quenched and aged condition, Figure 2(c). It is clear that at 500°C the effects of Mo and Nb are greatest in the quenched and aged condition.



<u>Figure 2</u> Strength Of Some Zirconium Alloys

(a) and (b) Annealed at 730°C (Ref. 4)

(c) β-quenched and aged (Ref. 5)

Increased strengthening is obtained in ternary alloys containing combinations of α- and β- stabilizing additions so that both solution and precipitation hardening contribute. Table I gives the tensile properties of some selected ternary and quaternary zirconium base alloys and indicates systems worth studying. Of these alloys it appears that the objectives may be reached by the ones containing 3 to 4 wt.% Sn and 1 to 2 wt.% Mo, or ones containing 1 to 2 wt.% Al and 0.5 to 1.5 wt.% Mo. From the limited number of creep results published it is not known how well the alloys will behave. Creep strength is not necessarily directly proportional to tensile strength in these alloys and is improved by alloying additions which provide intermetallic precipitates.

Table I

Tensile Properties of Various Zirconium Alloys, Normalized to 450°C

Alloy Composition, wt.%	Treatment	Test Temp. °C	U.T.S. kpsi	% Elong.	Reference
Zr-3 Al	Annealed at 650°C	20	112	10	(3)
		650	51.6	49	
		450_n*	64	~25	
Zr-3Al-3Sn	" "	20	127.2	10	(3)
		650	61.4	17	
		450_n	82	~10	
Zr-3Sn-1.5Mo	Air cooled from 900°C	20	143.3	2	(4)
		450_n	96	~10	
Zr-3.7Sn-2Mo	β-quenched/aged	500	105	10	(5)
		450_n	110	~10	
Zr-5Nb-2Sn	(α+β)q./aged 8 hours at 482°C	20	190	2	(6)
		450_n	130	~ 5	
Zr-1.5Al-1.5 Mo	Hot-worked and annealed at 790°C	565	54	27	(7)
		450_n	70	~20	
Zr-3Al-1.5 Sn-1.5Mo	" "	565	70	30	(7)
		450_n	90	~20	
Zr-1.5Al-1.07 Mo	Annealed at 785°C	450	85	30	(8)
Zr-1.5Al-0.5 Mo	(α+β) quenched	400	119	2	(9)
		450_n	112	2	

* n = normalized

TITANIUM ALLOY DEVELOPMENT

Intensive development programs in several countries have produced the current range of high strength titanium alloys for aircraft and aerospace applications. Starting with alloy systems analogous to those of zirconium, it has been possible to improve tensile and creep strength with increased complexity of composition. The elements Al, Sn, Mo, V and Si have generally higher solubility in titanium than in zirconium, but have similar effects on phase stabilization. Figure 3 shows the creep properties of a number of complex titanium alloys (10).

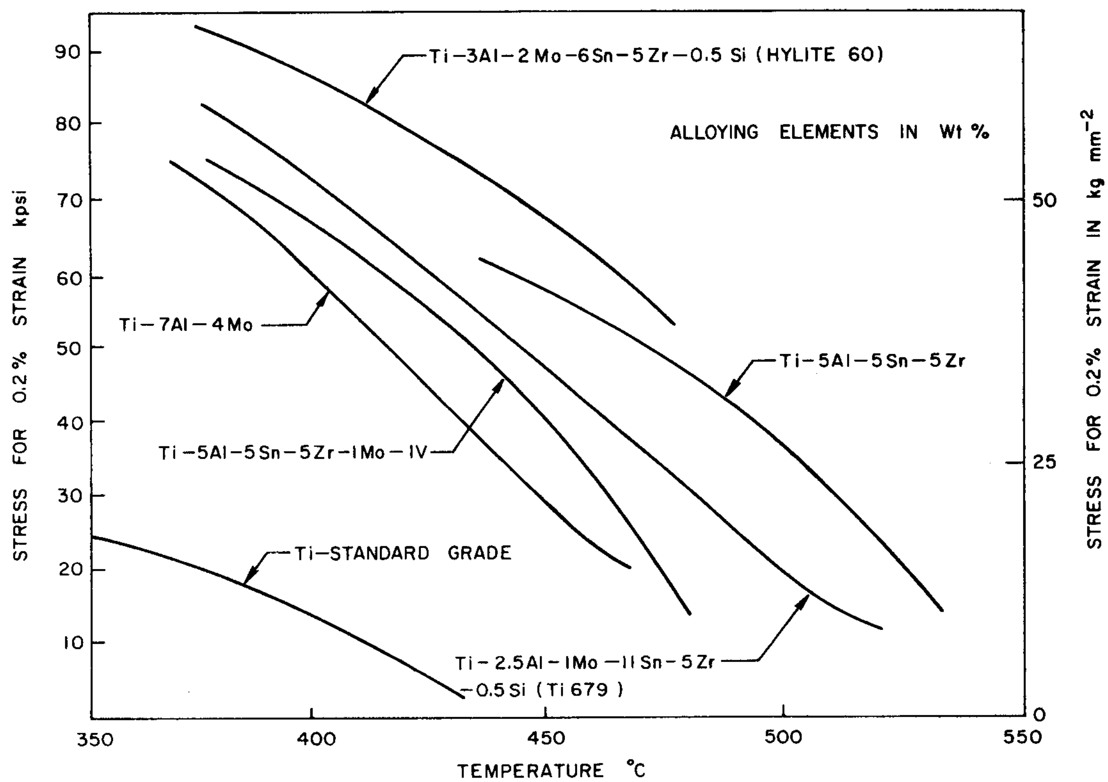


Figure 3 Stress To Give 0.2% Strain In 1000 Hours At 350-550°C In Titanium Alloys.

Ultimate tensile strengths of about 210 kpsi at 450°C are obtained for Hylite 60 and Ti 679. Thermal processing of these alloys is designed to exploit the solution - and precipitation - hardening contributions to strength by the alloying additions. The success of these development programs suggests that similar complex zirconium alloys should be possible. Attractive properties should be obtained from combinations of Sn, Mo, Nb and Al with the total amount of addition defined by the acceptable neutron cross-section.

NEUTRON CAPTURE CROSS-SECTION

Those who developed high strength titanium alloys were not concerned with neutron capture cross-section. However, zirconium alloys for power reactors must have as low a cross-section as possible and this severely restricts the choice and quantity of alloying additions. The thermal neutron capture cross-sections for alloying elements are given in Table II. The increment of cross-section for each 1% of alloying addition indicates the penalty in neutrons associated with each element.

Table II

(a) Calculated Thermal Neutron Capture Cross-sections

Alloy	Capture Cross-section Σ_c cm^2 per cm^3
Zr-3%Sn-1% Mo	0.0091
Zr-3%Sn-1%Mo-1%Nb	0.0095
Zircaloy-2	0.0087
Zr-2.5% Nb	0.0090

(b) Increase in Thermal Neutron Capture Cross-sections of Zirconium due to 1 wt.% Alloy Addition

Alloy	Cross-section Increase Σ_c cm^2 per cm^3
Sn	0.00019
Mo	0.00089
Nb	0.00037
V	0.00335
Sb	0.00174
Si	0.00114
Al	0.00012

THE DEVELOPMENT OF A HIGH TEMPERATURE ZIRCONIUM ALLOY

1. Selection of Solution Hardener

As indicated earlier, Al is a more effective strengthener than Sn. However, it is known that zirconium alloys containing Al have extremely poor corrosion resistance. Therefore, any pressure tube alloy containing significant amounts of Al (1 to 4 wt.%) would be dependent entirely on the perfection of its cladding to protect the alloy from the coolant. It has been shown in other investigations that good properties are obtainable with Sn and Mo additions. It is expected that Zr-Sn will have better corrosion resistance than Zr-Al and therefore will not be so dependent on the integrity of the cladding for protection. A Zr-3 Sn allloy was selected on this basis for an experimental series of complex alloys.

2. Selection of Alloy Composition

The limit set by neutron capture cross-section, the solubility limits of the individual elements and the prospect that good creep strength would be promoted by a composition giving intermetallic compounds, suggests the following range of alloys for experiment.

Zr with 2 to 4 wt.% Sn
plus 0.5 to 1.5 wt.% Mo
0.5 to 2 wt.% Nb
0.5 to 1.5 wt.% Al
0.5 wt.% Si.

The alloys should contain at least 1 wt.% of a β-stabilizer (Mo or Nb), with a greater range being possible for Nb than Mo because of its lower cross-section. Additions of Al and Si would be restricted to the minimum necessary to provide additional strength if the properties of a Zr-Mo-Sn-Nb alloy were inadequate.

3. Pressure Tube Cladding Material

Zirconium alloys with high temperature corrosion resistance have been developed elsewhere. The most promising alloy is a Zr-Cr-Fe alloy developed by the Vallecitos Laboratories of General Electric, U.S.A.[11]. Results on the alloy to date show adequate corrosion resistance to steam at 450°C and above.

4. Development Program

The objectives of the program are as follows:

(a) fabricate a small diameter tube (about 1-1/2") which can be installed in the high temperature X-4 steam loop in NRX by mid-1970.

(b) fabricate a full size (about 4" diameter) pressure tube which can be installed in the superheat loop of the NRU reactor by mid-1971,

(c) establish by late 1972 the production of pressure tubes that will meet the specifications for power reactors.

To accomplish these objectives in the projected time will demand a carefully coordinated program that will require the assistance of industry, universities and several divisions within AECL.

In general, the program will be as follows:

(a) the testing of material from small melts to determine mechanical properties, effect of irradiation and optimization of composition and heat treatment,

(b) fabrication of large ingots to provide material for mechanical testing and for the fabrication of pressure tubes,

(c) determination of in-reactor behaviour of pressure tubes,

(d) the establishment of a practical production process for pressure tubes.

EXPERIMENTAL RESULTS

The development program has already begun and some results are available.

1. <u>Age-hardening</u>

Figure 4 summarizes the age hardening behaviour of a number of alloys quenched from the β-phase; data for the Zr-2.5 wt.% Nb are included for comparison. The Zr-3 wt.% Sn alloys show a much stronger age-hardening reaction than conventional alloys.

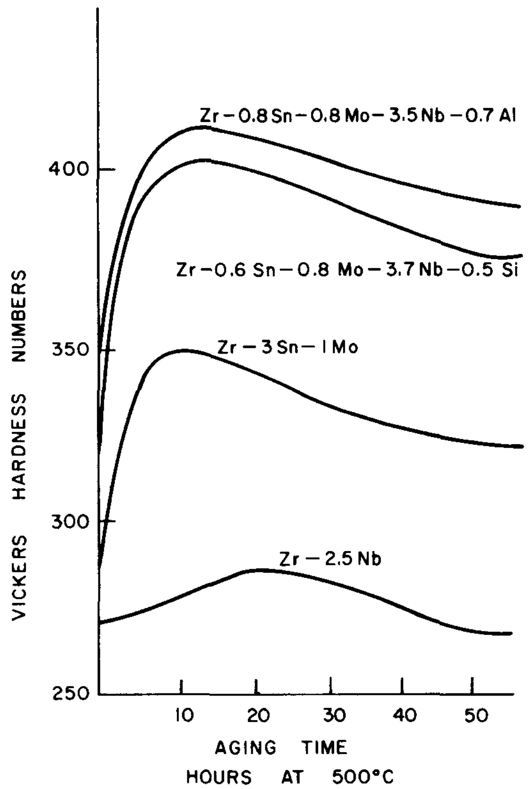


Figure 4 Age Hardening Of β-Quenched Complex Zr Alloys

2. Tensile Properties

The tensile test results for experimental alloys are given in Table III; included are results for Zr-2.5 wt.% Nb for comparison. The results show clearly the increased strength that can be produced in complex alloys. Experiments are being made to determine the properties of alloys in hot-worked and cold-worked-annealed conditions. These treatments may offer a better combination of strength and ductility than quench-aging for alloys containing 4 wt.% of the β-stabilizers Mo and Nb.

3. Stress Rupture Properties

Stress rupture tests at 400 to 500°C in air have produced the minimum creep rate results shown in Figure 5. For the Zr-3 wt.% Sn-1 wt.% Mo alloy, one laboratory test in helium at 450°C and at 12,000 psi has shown a decreasing creep rate reaching about 3×10^{-7} h^{-1} after 1200 h.

Table III

Tensile Test Results for Complex Zr-based Alloys

Alloy Composition Wt.%	Treatment	Test Temp. °C	0.2% Yield Stress kpsi	U.T.S. kpsi	% Elong.
Zr-3Sn-1Mo	(α+β)Q.aged	20	129.9	149.3	11
	24 hrs/500°C	400	90	103.0	11
Zr-3Sn-0.5Mo-2 Nb	(α+β)Q.aged	20	128	138	12
	24 hrs/500°C	450_n	82	90	12
Zr-3 Sn-0.8Mo-3.5Nb-0.7Al	(α+β)Q.aged	20	220	220	1
	6 hrs/525°C	450	133	143	1
Zr-3 Sn-0.8Mo--3.7Nb-0.7Si	(α+β)Q.aged	20	212	224	1
	6 hrs/525°C	450	136	144	1
Zr-2.5 Nb	(α+β)Q.aged	20	105	120	5
	24 hrs/500°C	450	52	65	8

n = normalized

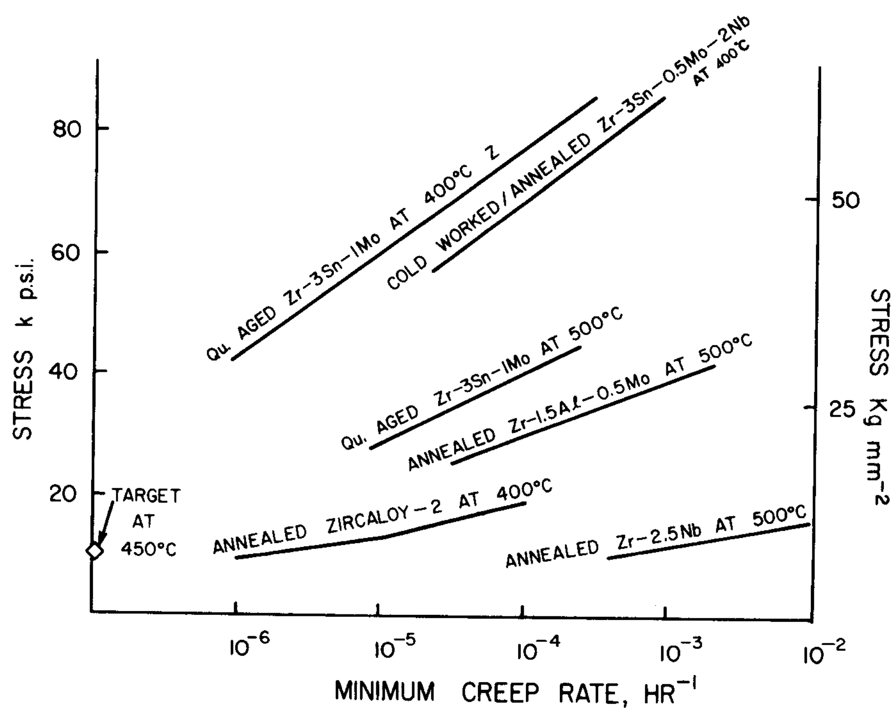


Figure 5 Stress Dependence Of Minimum Creep Rates For Complex Zr Alloys

4. Structural Analysis of the Alloy

The alloys are being studied by optical and electron microscopy and by X-ray diffraction analysis to provide an understanding of how the structure is related to properties. Examination of the alloys has shown that:

(a) the properties of the quench-aged alloys are dependent upon the decomposition of the β-phase. This process is very sensitive to composition and low ductility can result from certain quantities of addition.

(b) the martensitic structure resulting from the β-phase transformation is similar to that found in quenched Zr-2.5 wt.% Nb alloy. The age hardening response observed in Figure 4 is associated with high densities of precipitate although the reaction product has not been identified yet.

(c) the structural form of the heat-treated alloy appears to be stable at 400°C to 500°C with the precipitate stability enhanced by aging at temperatures at 525 to 550°C.

(d) cold work followed by annealing treatments produces a subgrain structure similar to that formed in conventional zirconium alloys after similar heat treatments.

CONCLUSIONS

From our assessment and the experimental work to date it can be concluded that a zirconium alloy for pressure tubes at temperatures of 450°C and above appears feasible. The alloy will be complex and will have a composition within the following ranges of alloying additions

2 to 4 wt.% Sn
0.5 to 1.5 wt.% Mo
0.5 to 2 wt.% Nb
0.5 to 1.5 wt.% Al
0.5 wt.% Si

It is expected that the alloy will have a neutron capture cross-section not greater than 10% more than Zircaloy-2 and capable of design stresses of 10 to 12 kpsi at 450°C.

ACKNOWLEDGEMENTS

I am very grateful to Dr. C.D. Williams for the indispensible discussions and help in preparing this paper. I thank all my colleagues for their assistance and contributions.

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