Fabrication and Corrosion Properties of V-(4-20)Cr-4Ti alloys

T. Sakamoto, M. Fujiwara, M. Satou and K. Abe

Department of Quantum Science and Energy Engineering,
Graduate School of Engineering, Tohoku University, Sendai, Japan

Introduction: Corrosion resistance

Compatibility with water (for coolant)

- **Water-cooling system for high-heat flux components of fusion reactors**
- **Reaction estimation between vanadium alloys and water for safety assessment of fusion components**
- **Non-fusion application including fission reactors**

It is necessary to estimate corrosion behavior of vanadium alloys in high-temperature/ pressurized water.

Experimental Procedure

Alloy Preparation

* collaboration with IMR/Tohoku Univ.

1st heat	・V-15Cr-4Ti	・V-15Cr-4Ti-0.5Y		
	・V-25Cr-4Ti	・V-25Cr-4Ti-0.5Y		
2nd heat	・V-4Cr-4Ti	・V-7Cr-4Ti	・V-10Cr-4Ti	・V-12Cr-4Ti
	・V-15Cr-4Ti	・V-20Cr-4Ti	・V-25Cr-4Ti	

Melting Procedure

1. Before melting

V：Pre-refined by EBM (Electron Beam Melting)

Ti：Degassed by arc melting and pre-refined by EBM

Cr：High-purity Cr

2. Melting

Arc melting, atmosphere：in Ar

→Impurities reduction by using EB-melted vanadium for getter

3. Fabrication procedure

- Ingot after melting (d:30mm, t:8mm)
- 1300℃ hot-vacuum forging (t:4mm)

  →200℃ hot roll (t:1.0mm), →cold roll (t:0.25mm)

EBM apparatus

Arc melting apparatus

Experimental Procedure

Annealing

- Temp.：900, 1000, 1100, 1200, 1300℃
- Time：1, 2h
- Vacuum：1×10^{-5}torr

Tensile test (at RT)

- Strain rate：$6.7\times10^{-4}s^{-1}$
- Specimens: Small-size tensile specimen (gauge: 5×1.2×0.25mm)
- Fracture surface cxamination by SEM

Charpy impact test

- Specimens: Small-size Charpy test specimen : 20×1.5×1.5 mm
- Temp.：-196 ～ 200 ℃
- Test speed：5 m/s
- Fracture surface examination by SEM

Experimental Procedure

Corrosion test in high-temperature-pressurized water

- Specimen：Coupon specimen(10 x 15 x 1mm),
  Small-size tensile specimen (gauge：5.0 x 1.2 x 0.25mm)
- Apparatus: Autoclave for PWR environment test
- Condition：288℃, 85atm., 300h, dissolved-oxygen : 400 ppb

Corrosion test in high-temperature steam

- Specimen：Small-size tensile specimen (gauge：5.0 x 1.2 x 0.25mm)
- Apparatus: Autoclave for acceleration test for zirconium alloys
- Condition ：400℃, 105atm., 72h

After corrosion test

- Measurement of weight change
- Tensile test at RT
- SEM observation

Result: Chemical composition

1st heat

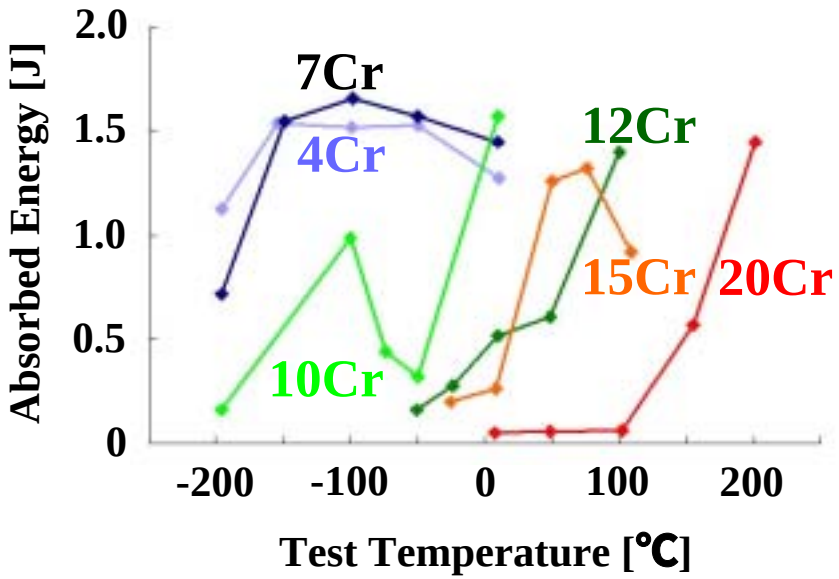
	(wt%)					(wppm)			
	Cr	Ti	Si	Al	Y	C	O	N	H
PURE V	0.016	<0.001	0.047	<0.006	<0.0005	185	88	646	4
V-15Cr-4Ti	14.75	4.145	0.225	0.015	<0.0005	224	171	673	9
V-15Cr-4Ti-0.5Y	14.15	3.880	0.165	<0.006	0.4980	261	344	618	37
NIFS HEAT 1	4.1	4.4	0.020	-	-	67	181	88	18
V-4Cr-4Ti	3.885	3.940	0.049	<0.006	<0.0005	217	112	604	7
V-4Cr-4Ti-0.5Y	4.010	4.025	0.050	<0.006	0.502	278	89	604	10

2nd heat

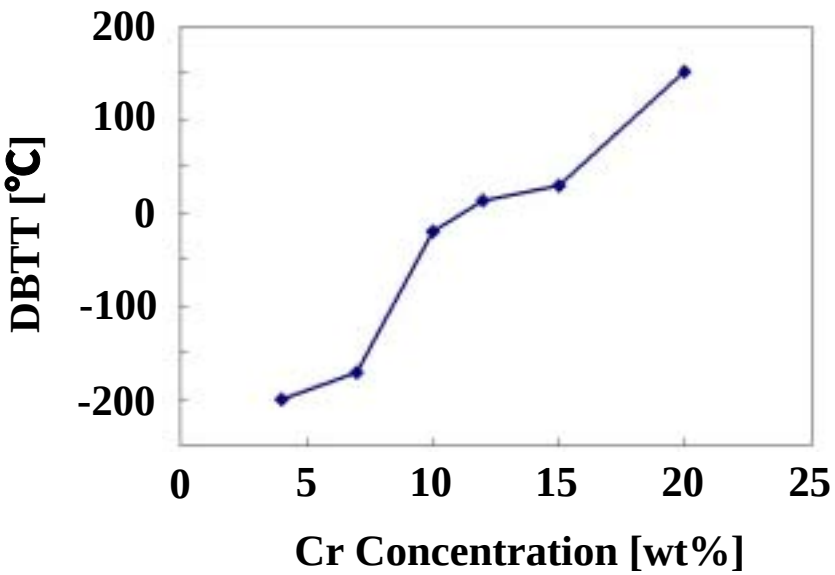
	(wt%)					(wppm)			
	Cr	Ti	Si	Al	Y	C	O	N	H
PURE V	<0.001	<0.001	-	0.0215	<0.001	37	249	221	6
V-4Cr-4Ti	4.275	4.250	-	0.0480	<0.001	93	235	171	5
V-7Cr-4Ti	7.170	3.650	-	0.0410	<0.001	71	213	174	9
V-10Cr-4Ti	10.55	4.145	-	0.0450	<0.001	118	276	249	11
V-12Cr-4Ti	12.25	4.095	-	0.0375	<0.001	186	304	485	15
V-15Cr-4Ti	14.46	3.950	-	0.0360	<0.001	240	273	382	12
V-20Cr-4Ti	20.10	4.120		0.0365	<0.001	165	233	220	5

Result: Charpy impact test

Absorbed Energy

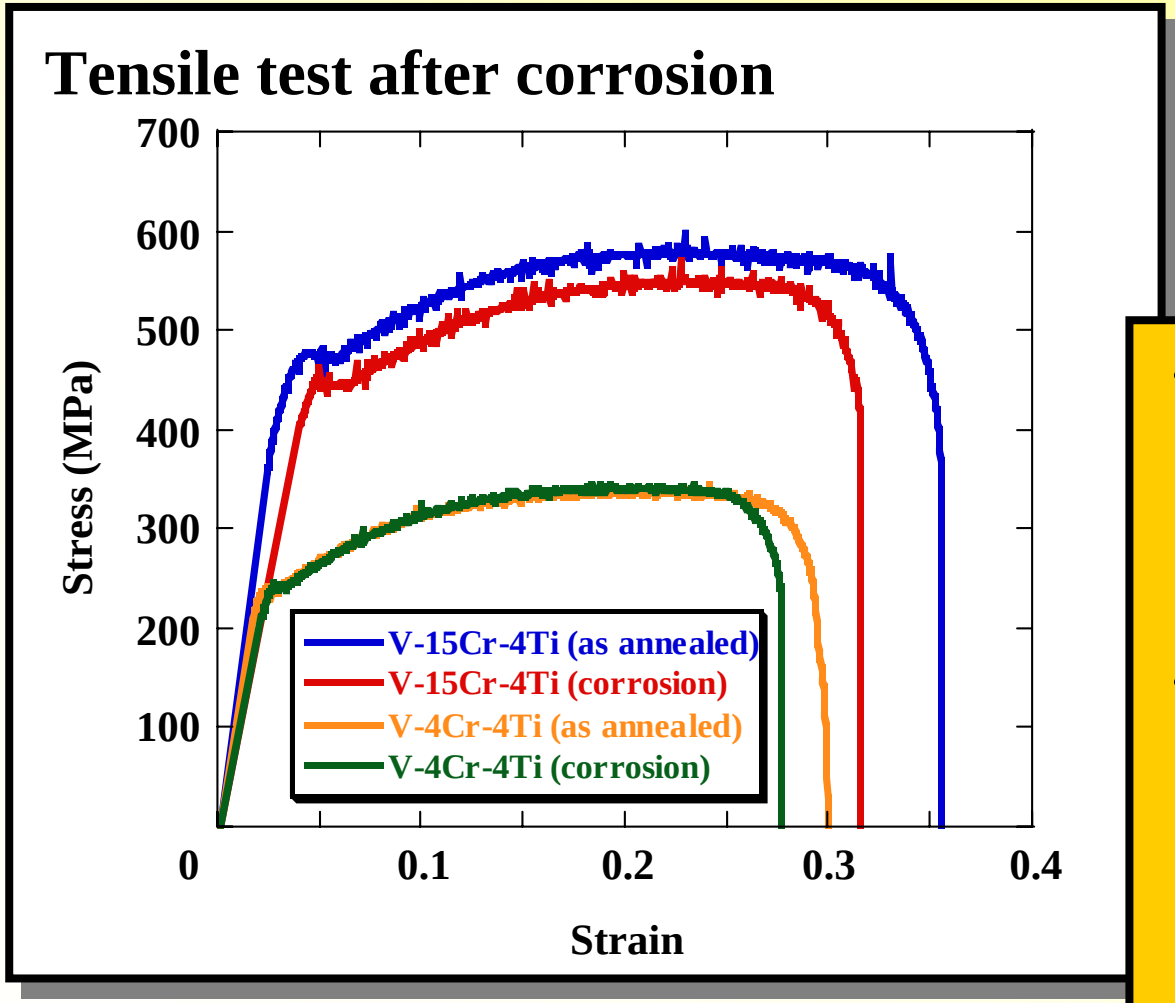


DBTT vs Cr concentration



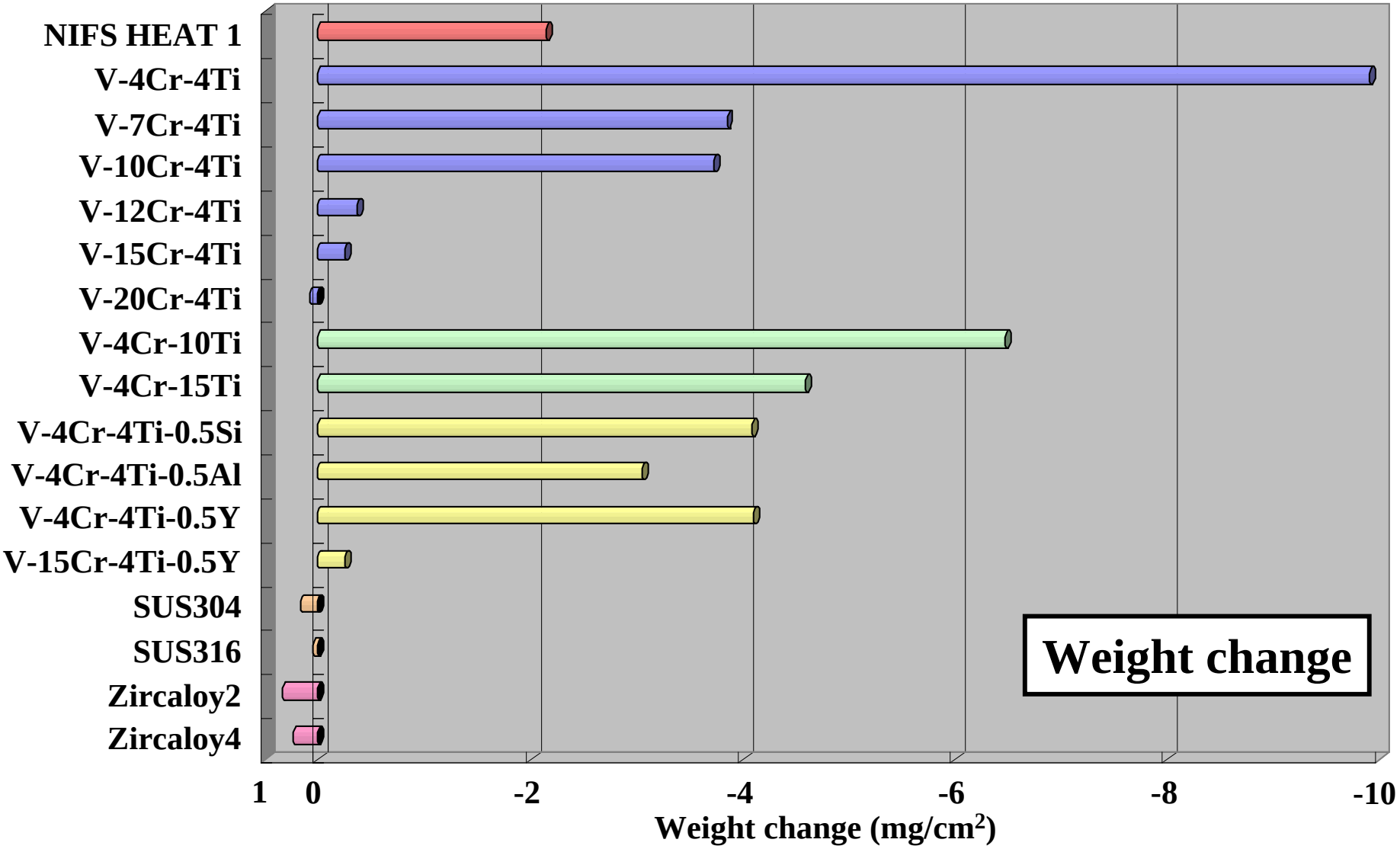
- Up to 10% Cr, the alloys showed ductility at RT.
- DBTT increased linearly with increasing Cr concentration.

Result: Corrosion test in high-temperature-pressurized water

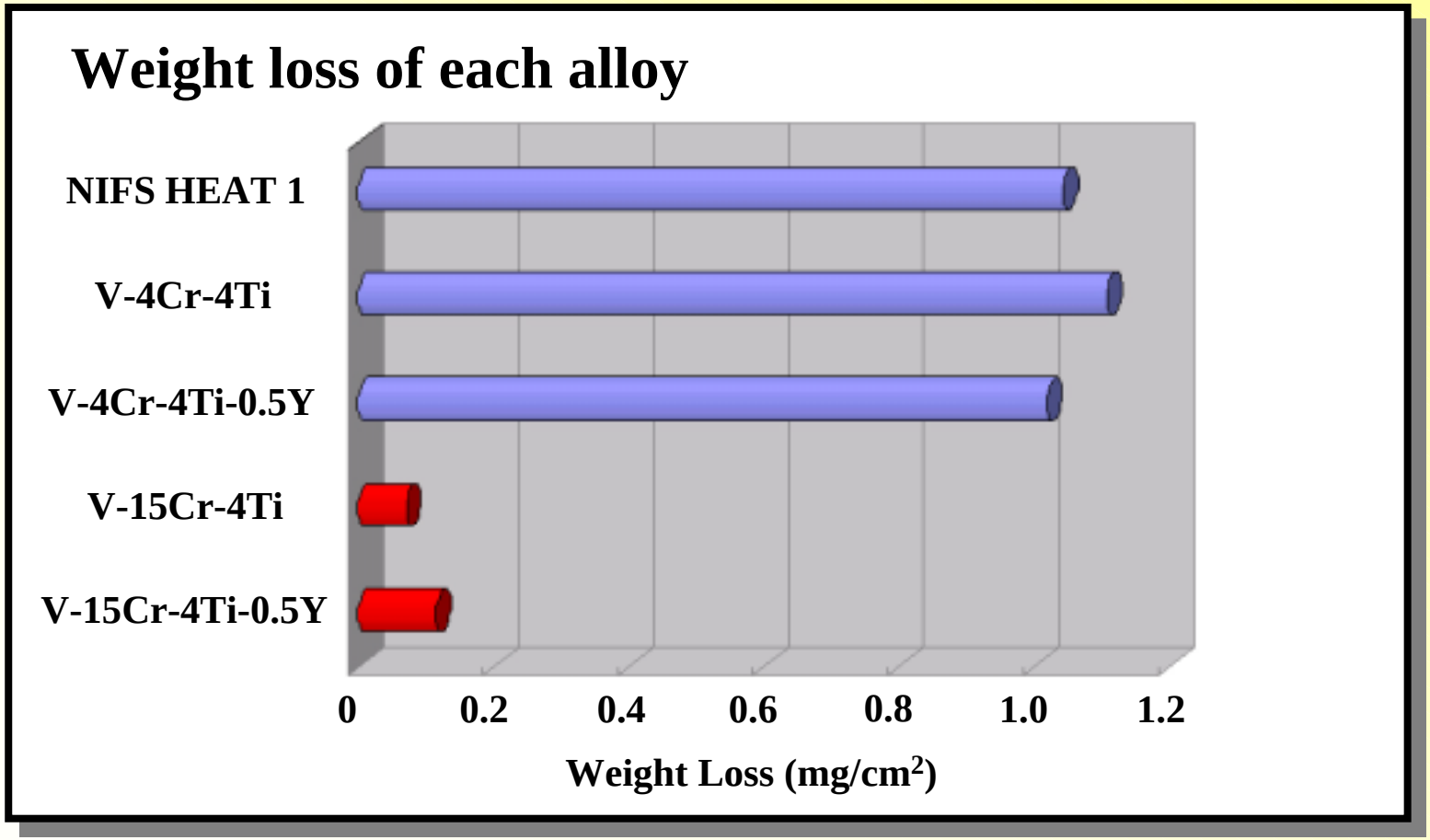


- Yield stress, tensile strength and elongation were almost equal before and after corrosion treatment.
- V-15Cr-4Ti alloy
  1. Total elongation of this alloy was as long as that of V-4Cr-4Ti alloy.
  2. Tensile strength of this alloy was larger than that of V-4Cr-4Ti alloy.

Result: Corrosion test in high-temperature steam

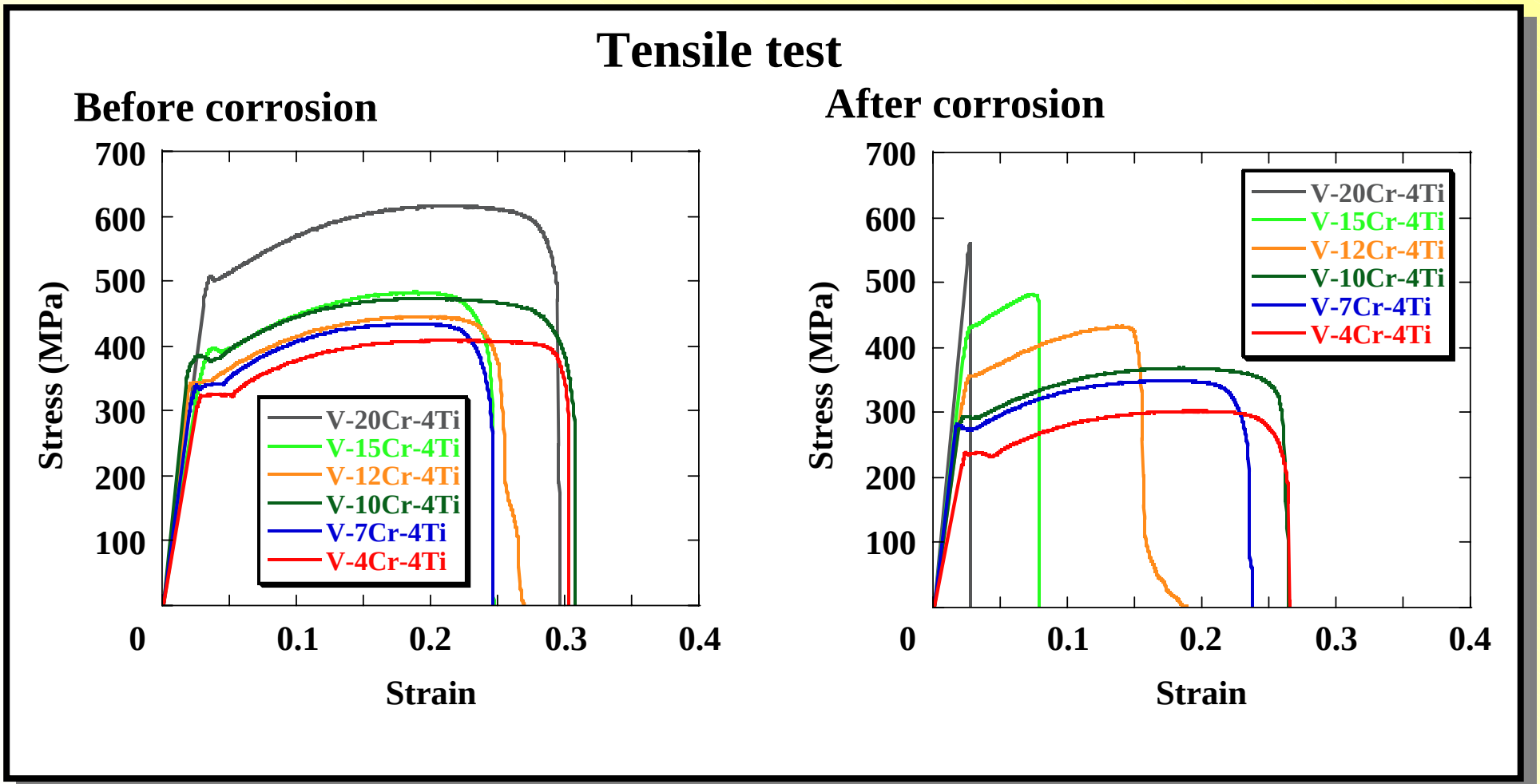


Result: Corrosion test in high-temperature pressurized water



- Weight loss of V-4Cr-4Ti type alloys more than 1.0mg/cm^2
- Weight loss of V-15Cr-4Ti type alloys less than 0.2mg/cm^2

Result: Corrosion test in high-temperature steam



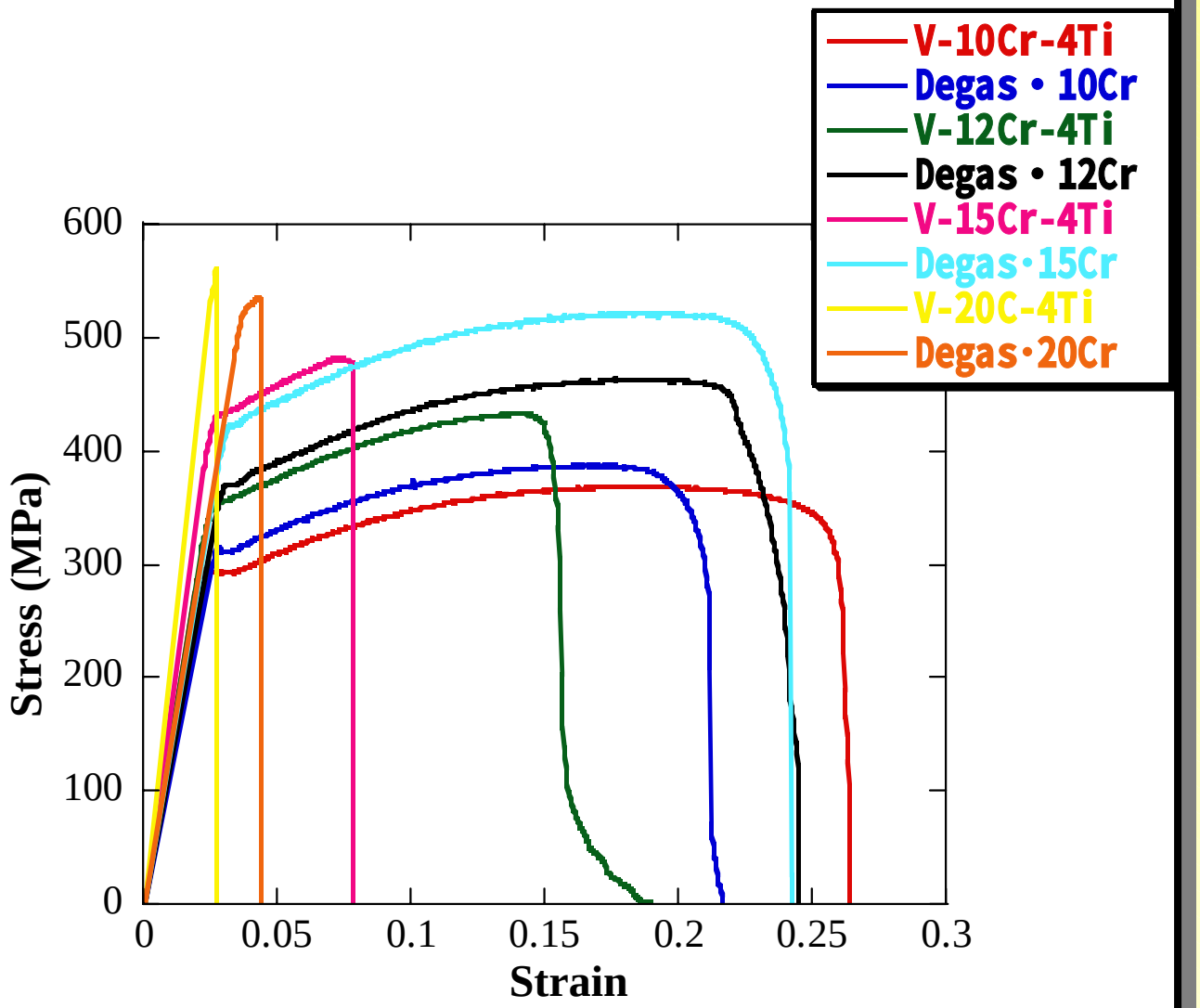
Result: Corrosion test in high-temperature steam

Tensile test after corrosion

More than 12% Cr, strain decreased significantly after corrosion.
→Embrittlement for H

Annealing for degas of H
Condition：
500℃, 1h, $3x10^{-2}$Pa

After annealing, the strain of V-(12, 15)Cr-4Ti alloy were recovered.



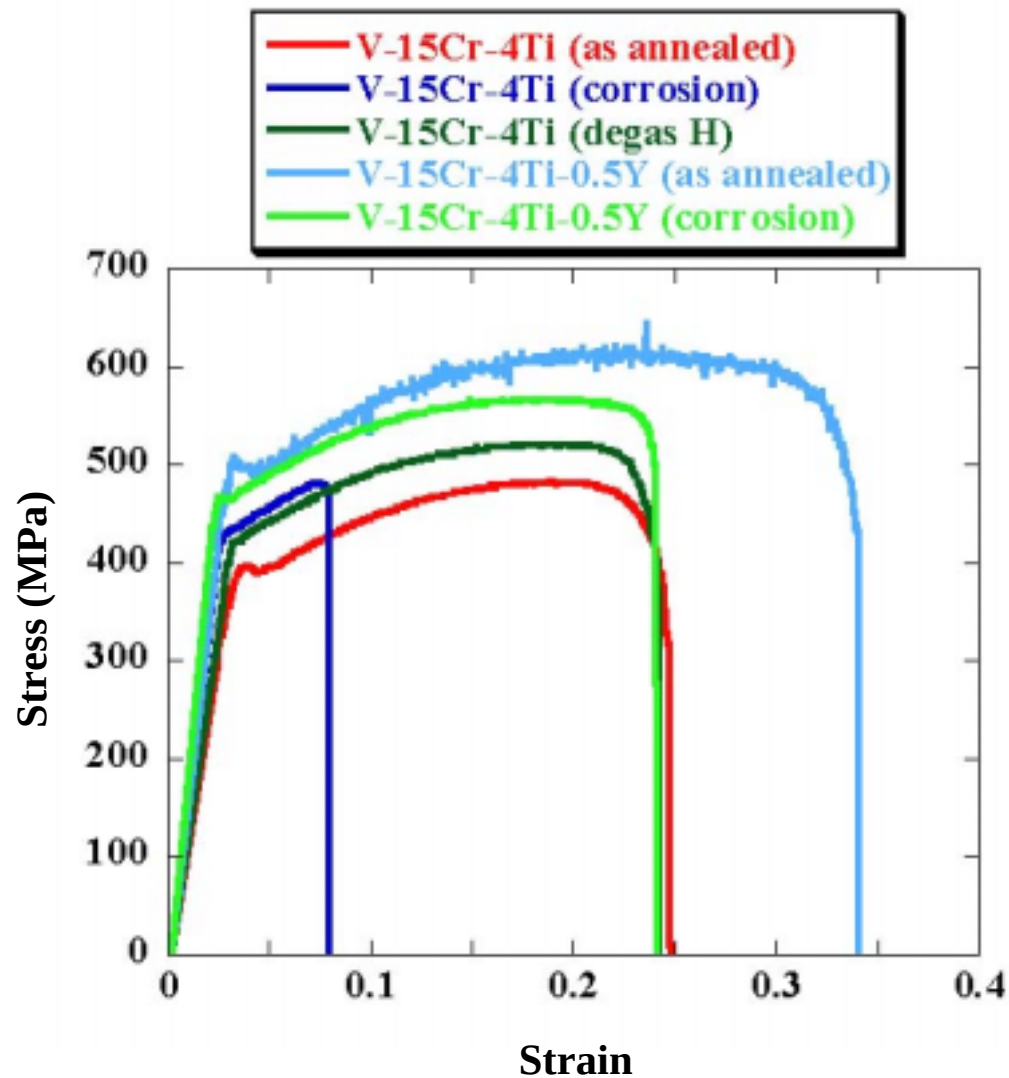
Result: Corrosion test in high-temperature steam

Tensile test after corrosion

Effect of Y addition for V-15Cr-4Ti type alloy

- **V-15Cr-4Ti alloy :**
  Strain was recovered after degassing.
- **V-15Cr-4Ti alloy :**
  Strain was almost same before and after degassing.

→The doping of Y was effective at control of embrittlement for H.



Summary

Development of high-Cr V based alloy

1. Impurities
   - The impurity contamination was almost depressed during alloy melting.
2. DBTT
   - Up to 10% Cr, the alloys showed ductility at RT.
   - DBTT increased linearly with increasing Cr concentration.

Corrosion properties of high-Cr V-Cr-Ti type alloys

- Weight changes of V-(12-20)Cr-4Ti type alloys were significantly less than that of V-4Cr-4Ti type alloys.
- Alloying with above 12% Cr, strain decreased significantly after corrosion; H may induce embrittlement. The doping of Y can be effective to reduce embrittlement.

Oxidation and Mechanical Properties of V-4Cr-(4-15)Ti alloys

K. Takanashi, M. Fujiwara, M. Satou and K. Abe

Department of Quantum Science and Energy Engineering,
Graduate School of Engineering, Tohoku University, Sendai, Japan

Introduction: Corrosion resistance

V-4Cr-4Ti alloy

High-Cr alloy

improve corrosion resistance

Corrosion resistance was improved by protective oxides in high temperature-pressurized water

V-4Cr-4Ti-Si,Al,Y alloy

improve oxidation resistance

Si:formation of stable inner oxides
Al:absorb oxygen preferentially
Y:suppress oxides growth, diffusion of oxygen

High-Ti alloy

improve oxidation resistance (V-Ti alloys)

- **improve oxidation resistance by increase Ti concentration**
- **expecting corrosion resistance by formation of TiN in liquid Li**

Objective:

The objective of this study is to prepare V-based high Ti alloys with V-4Cr-4Ti alloy as a reference and to study the influence of Ti content on mechanical properties and oxidation behavior of these alloys for improvement of corrosion resistance of V-based alloys.

This report presents the oxidation behavior in air.

Experimental procedure 1

Alloy preparation

* collaboration with IMR Tohoku Univ.

1. **Electron beam (EB) melting**

   V and Ti were melted by electron beam to remove impurities

2. **Arc melting**

3. **Rolling**

compositions(wt.%)
- V-4Cr-4Ti
- V-4Cr-10Ti
- V-4Cr-15Ti

hot-vacuum-forging → hot roll → cold roll

1300℃-vacuum forged to 4mm

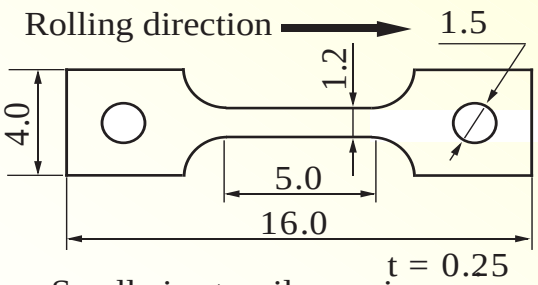
200℃ oil-bath rolled to 1mm

rolled to 0.25mm

V-4Cr-4Ti :good workability→started from hot roll

V-4Cr-10Ti
V-4Cr-15Ti :workability unknown→started from hot-vacuum forging

4. **specimens**



Small-size tensile specimen
(unit : mm)

Experimental procedure 2

Annealing

V-4Cr-4Ti V-4Cr-10Ti V-4Cr-15Ti	Temp.:1000℃ Time:1h Vacuum:10^{-5}Torr

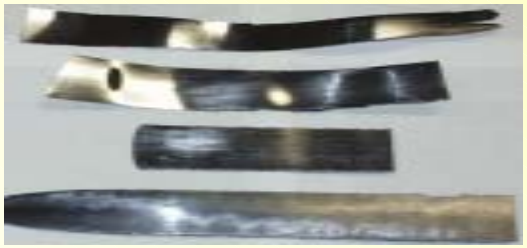
Oxidation test in air

Temp.：500,600,700,750℃
Time：1h
- High temperature,vacuum:10^{-4}Torr ⇒ exposure
- Weight and thickness changes were measured.
- Composition of oxide layers were identified by X-ray diffraction analysis.

Tensile testing (at R.T.)

- Strain rate：$6.7 \times 10^{-4} s^{-1}$
- Fracture surfaces were examined by SEM

Results: Preparing alloys



V-4Cr-4Ti

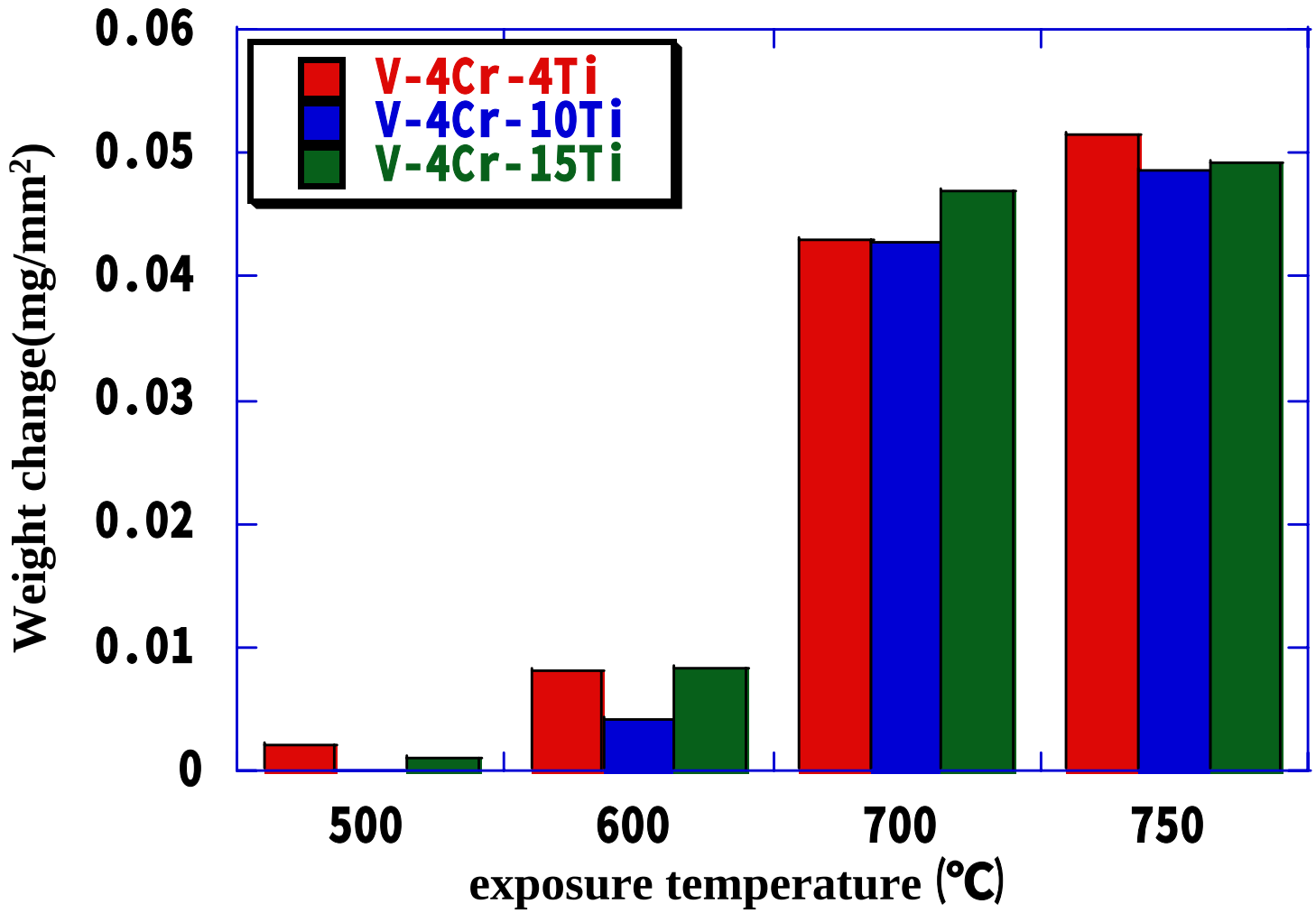
V-4Cr-10Ti

V-4Cr-15Ti

compositions(wt.%)

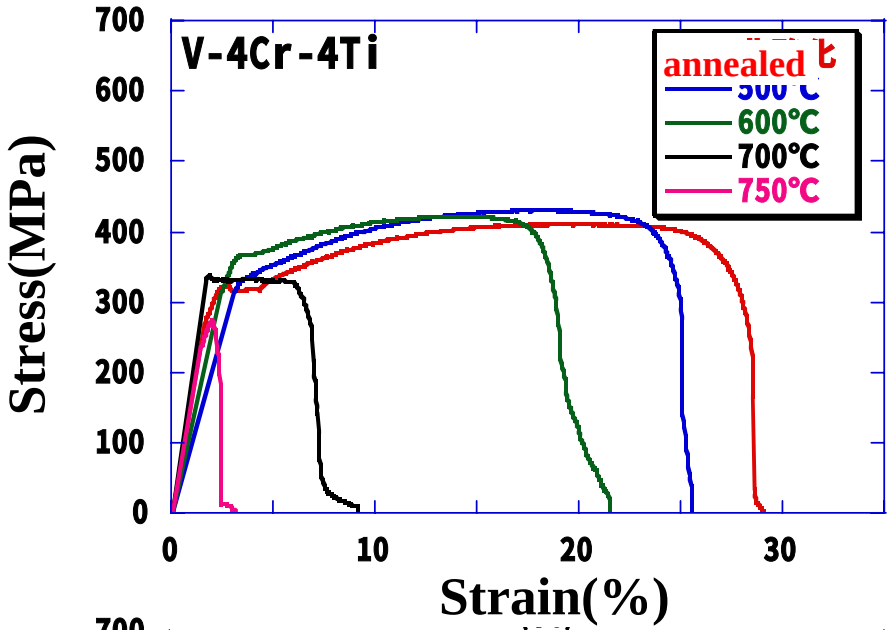
	V	Cr	Ti	Si	Al	Y	C	O	N	H
V-4Cr-4Ti	Bal.	4.275	4.250	-	0.048	0.001	0.0093	0.0235	0.0171	0.0005
V-4Cr-10Ti	Bal.	4.215	9.755	-	0.110	0.001	0.0214	0.0275	0.0314	0.0004
V-4Cr-15Ti	Bal.	4.040	14.40	-	0.163	0.001	0.0227	0.0323	0.0282	0.0005
NIFS-HEAT-1	Bal.	4.1	4.4	-	-	-	0.0067	0.0181	0.0088	0.0018

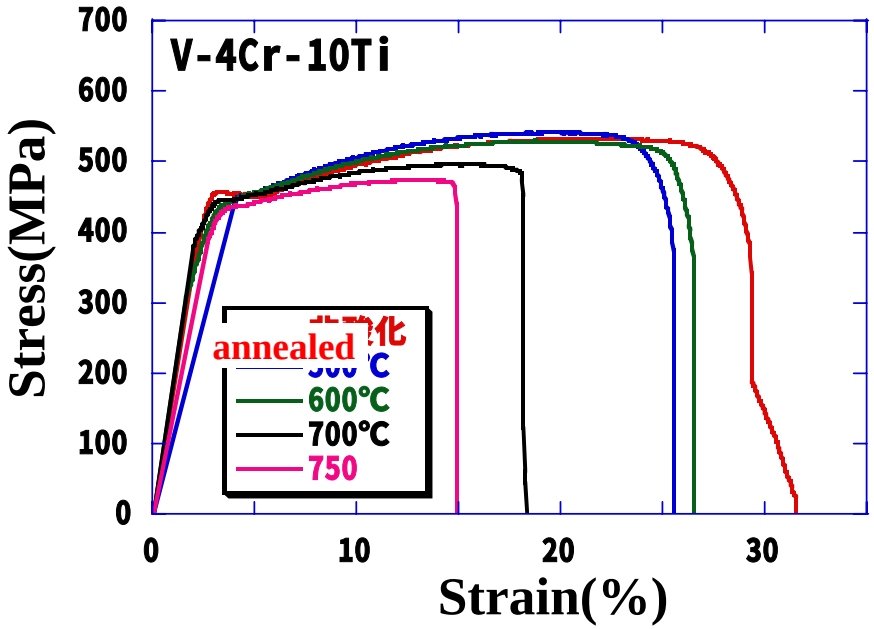
Results: Weight change after oxidation

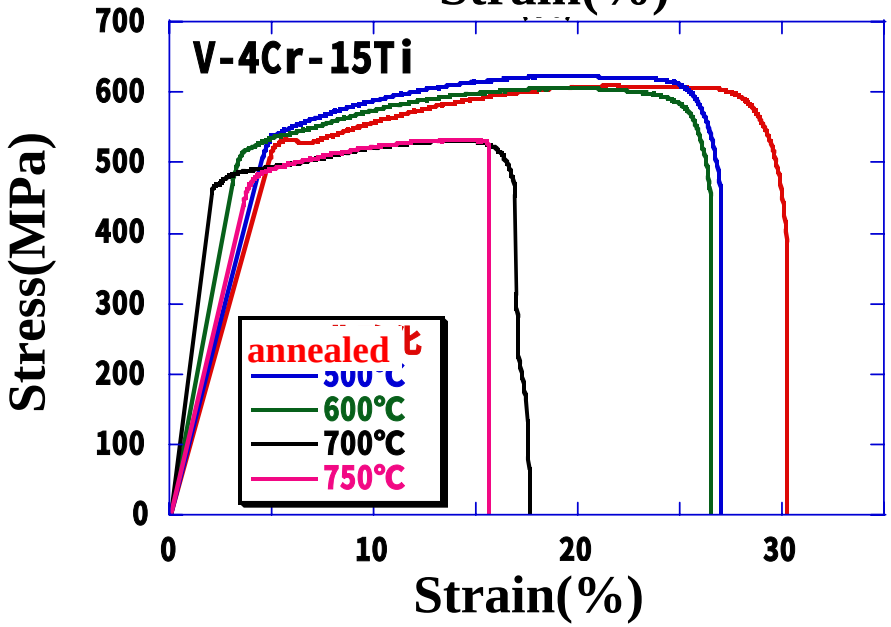


- Weight increase of each alloy was significant over 700℃.
- Ti concentration had little or no effect on weight change.

Results: Tensile properties





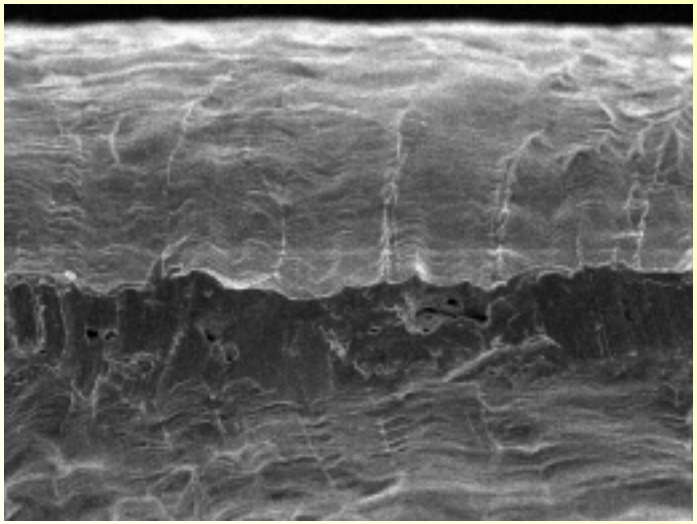


V-4Cr-4Ti:
Elongation decreased significantly over 700℃.

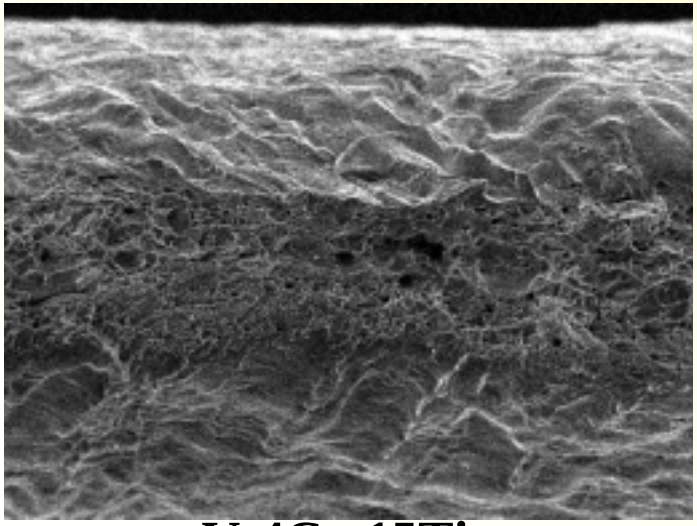
V-4Cr-(10,15)Ti:
Elongation > 15% was maintained over 700℃.

Results: SEM observations

annealed

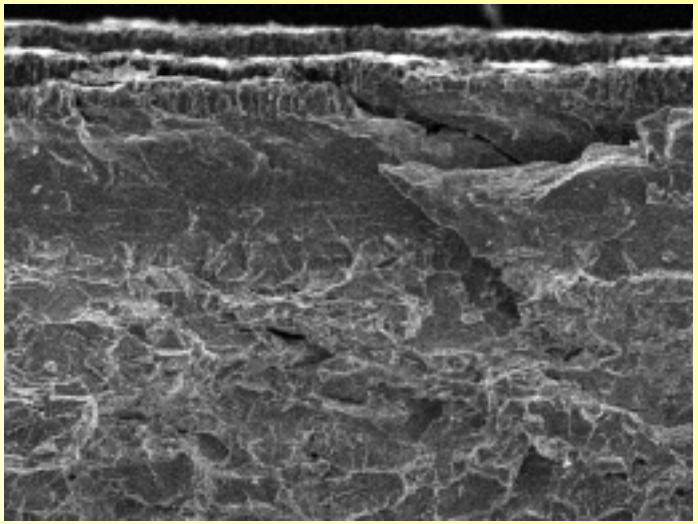


V-4Cr-4Ti



V-4Cr-15Ti

750℃-1h exposure

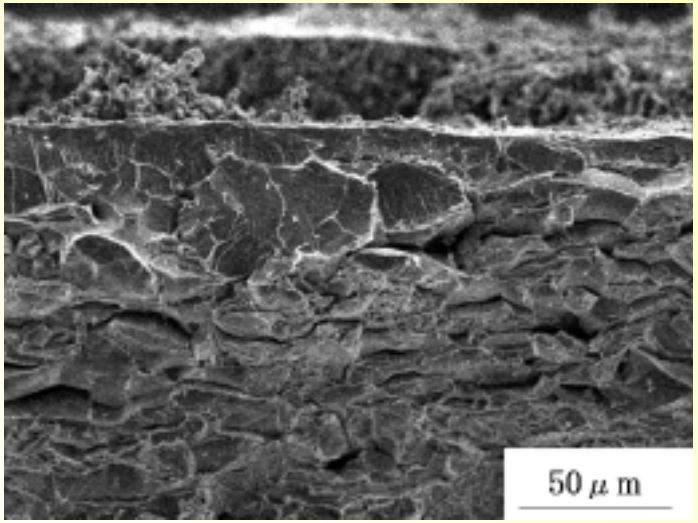


V-4Cr-4Ti

oxide layer

cleavage fracture

ductile fracture



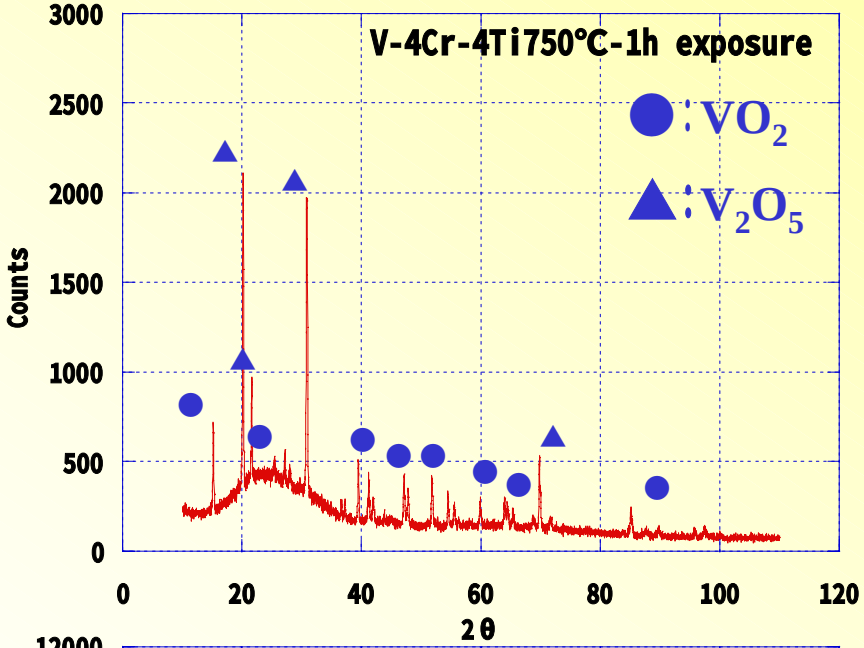
V-4Cr-15Ti

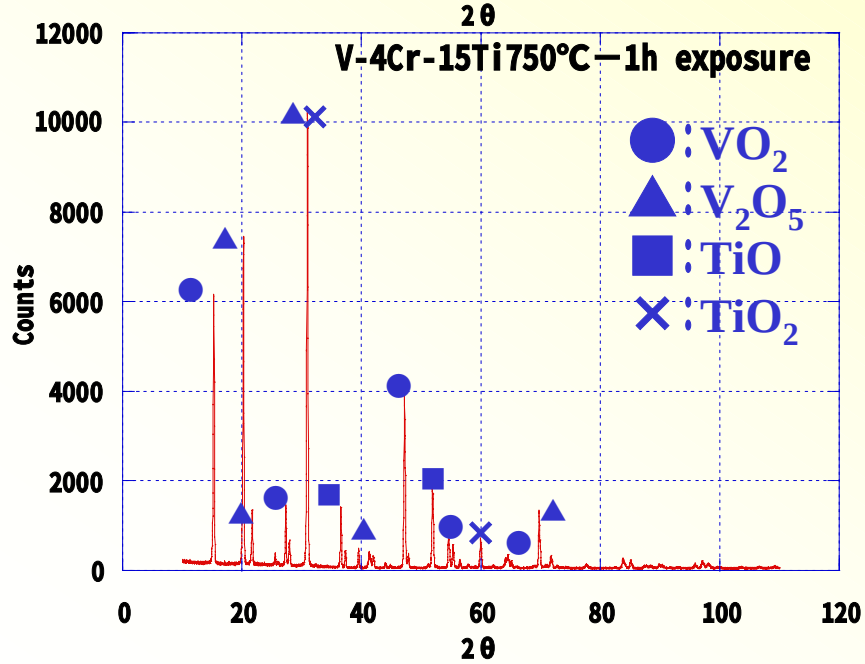
oxide layer

cleavage fracture

ductile fracture

Results: Identify of oxide layers by X-ray diffraction



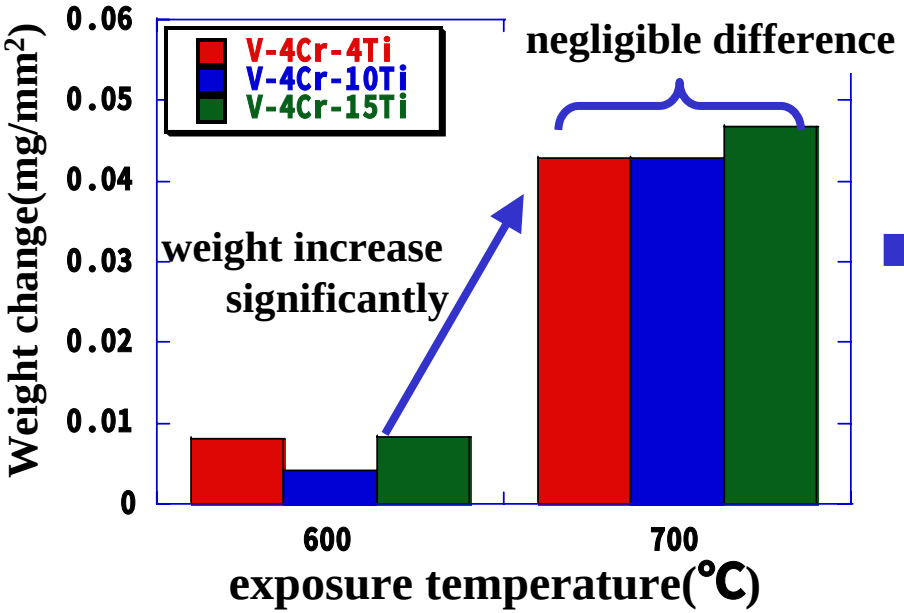


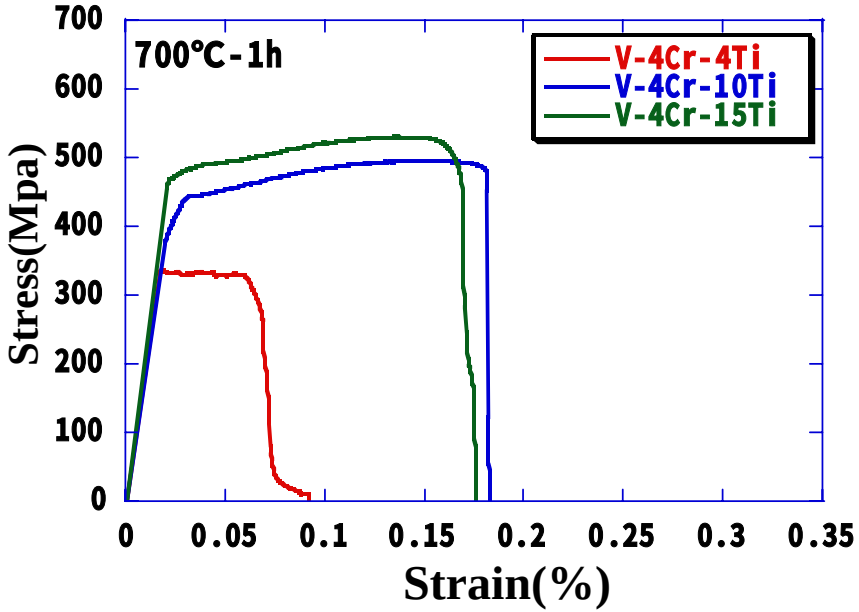
The ratio of peak

	VO_2 : V_2O_5
V-4Cr-4Ti	2:7
V-4Cr-15Ti	5:6

- V-4Cr-4Ti
  Oxide layer was predominantly V_2O_5.
- V-4Cr-15Ti
  VO_2 increased.
  TiO was formed.

Discussion: Influence of Ti concentration to oxide layer





- **Changes of composition and property of oxide layer**
  Growth of V_2O_5 was suppressed and stable VO_2 was formed in high-Ti alloys.
- **Changes of internal fracture behavior**
  Oxygen diffusion might decrease as growth of V_2O_5 was suppressed.

Summary

- **Alloy Preparation**

Each alloy showed good workability.
Interstitial impurities might be decreased by using V,Cr and Ti with high purity.

- **Influence of Ti concentration on air exposure**

Weight of each alloy increased significantly over 700℃.
Growth of V_2O_5 phase in oxide layer was suppressed with increasing Ti concentration.

- **Influence of Ti concentration on tensile property**

High-Ti alloys showed larger elongation after 700/750℃exposure than V-4Cr-4Ti alloy.