

MODIFICATION OF THE INCLUSIONS IN AUSTENITIC STAINLESS STEEL BY ADDING TELLURIUM AND ZIRCONIUM

MODIFIKACIJA VKLJUČKOV V AVSTENITNEM NERJAVNEM JEKLU Z DODAJANJEM TELURJA IN CIRKONIJA

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Prejem rokopisa – received: 2015-09-18; sprejem za objavo – accepted for publication: 2016-09-02

doi:10.17222/mit.2015.297

The control of the formation of non-metallic inclusions and the characterization represents the basis for the improvement of steel product properties and leads to sustainable development in the design of new steel grades. In order to produce steels with better machinability, such as AISI 303 grades, a modification of inclusions with a carefully designed chemical composition is presented. The aim of the research was to examine the possibility of increasing the effect of machinability of AISI 303 stainless-steel micro-alloying by tellurium and zirconium. In this work we present detailed SEM/EDS analyses of the modified non-metallic inclusions – manganese sulphides. In AISI 303 steel alloyed with Te and Zr the inclusions consisted of complex particles with more spherical shapes effectively acting as shaving breakers. For this reason the AISI 303 modified grades have better machinability compared to the standard AISI 303 grade and with mechanical properties within the limits prescribed for AISI 303 standard grade.

Keywords: stainless steel, machinability, inclusions, manganese sulphides, tellurium, zirconium

Kontrola tvorbe nekovinskih vključkov in njihova karakterizacija predstavljata osnovo za izboljšanje lastnosti jeklenih proizvodov in vodita k trajnostnemu razvoju novih vrst jekel. Predstavljena je modifikacija vključkov s skrbno načrtovano kemijsko sestavo z namenom izdelave jekel z boljšo obdelovalnostjo, kot je AISI 303. Namen raziskave je bil raziskati možnost izboljšanja obdelovalnosti nerjavnega jekla AISI 303, mikrolegiranega s telurjem in cirkonijem. V delu so predstavljene podrobne SEM/EDS analize modificiranih nekovinskih vključkov – manganovih sulfidov. V jeklu AISI 303, legiranem s Te in Zr, delujejo vključki, sestavljeni iz kompleksnih delcev sferične oblike, kot učinkoviti lomilci ostružkov. To je razlog, da ima modificirano jeklo AISI 303 boljšo obdelovalnost v primerjavi s standardnim jeklom AISI 303 in mehanske lastnosti v mejah, ki so predpisane za standardno jeklo AISI 303.

Ključne besede: nerjavno jeklo, obdelovalnost, vključki, manganovi sulfidi, telur, cirkonij

1 INTRODUCTION

Stainless steel plays an important role in all emerging technologies. Stainless steel type 1.4305 is popularly known as grade AISI 303 stainless steel. Grade AISI 303 is the most readily machineable of all the austenitic grades of stainless steel. The machineable nature of grade AISI 303 is due to the presence of sulphur in the steel composition.

The AISI 303 stainless steel referred to as "free-machining" stainless steel has the following nominal chemical composition, **Table 1**.¹

Table 1: Chemical composition of standard AISI 303 austenitic stainless steel, in mass fractions (wt%)

Tabela 1: Kemijska sestava standardnih AISI 303 avstenitnih nerjavnih jekel, v masnih odstotkih (wt%)

C	Mn	Si	Cr	Ni	P	S
0.15	2.00	1.00	17.0-19.0	8.0-10.0	0.2	0.15 min

The MnS stringers help to promote the easy breakup of metal shavings during machining.^{2,3} And while the

sulphur improves the machining, it also causes a decrease in the corrosion resistance⁴ and a slight lowering of the toughness and a general decrease of the mechanical properties.

The intention is to make higher machinability of this steel grade, but with good mechanical properties. The results show that after micro-alloying with tellurium or zirconium the modification of non-metallic inclusions – manganese sulphide of AISI 303 stainless steel – can be significantly changed. The machinability varies with the inclusion shape, which means that it is desirable that the manganese sulphide inclusions in steel must be as spherical as possible.²

The aim of the research was to examine the possibility of reducing the effect of sulphur on the mechanical properties of AISI 303 by micro-alloying with tellurium and zirconium, which can modify the MnS and improve the machinability, with mechanical properties within the limits prescribed for AISI 303 standard grade.

2 EXPERIMENTAL PART

The detrimental effects of inclusions in steel do not only depend on their sizes, shape, distribution, but also on their chemical composition and mechanical properties. For this reason, the control of the formation of non-metallic inclusions and the characterization represent the basis for the improvement of steel product properties and lead to sustainable development in the design of new steel grades.

The Thermo-Calc software package is used to show the temperature region where in theoretical way it is possible to form non-metallic inclusions. Also, it has to be taken into consideration that Thermo-Calc calculation is related to equilibrium state and is also related to global chemical steel composition, in this case of standard AISI 303.

The aim of the research was to examine the possibility of increasing the effect of machinability of AISI 303 stainless steel by micro-alloying with tellurium and zirconium. They seem to exert beneficial effects by promoting the retention of globular-shaped sulphide type inclusions.⁵

The intention is to make better machinability of AISI 303 stainless steel and to keep good mechanical properties. Tellurium or zirconium are considered to have a less deleterious effect than sulphur on the mechanical properties.

The production of AISI 303 stainless steel micro-alloyed by tellurium and zirconium was performed in a vacuum induction furnace with capacity of 20 kg at the Metallurgical Institute "Kemal Kapetanović" in Zenica. The ingots were processed by forging, hot rolling and heat treatment.

Two types of modified steel based on AISI 303 were used, the one modified by Te, and the other modified by Te and Zr, **Table 2**.

In order to prepare a sample, grinding and polishing of the testing samples were carried out. Then the analysis of the content, size and distribution of non-metallic inclusions in the unetched state was carried out at the Metallurgical Institute of Zenica, Bosnia and Herzegovina.

The detailed SEM/EDS analyses of modified non-metallic inclusions were performed by scanning electron microscope (SEM) Jeol JSM 5610 with attached energy-dispersive x-ray spectroscopy (EDS) system Gresham Scientific Instruments Ltd., Model Sirius 10/SUTW at an accelerating voltage of 15 kV at the

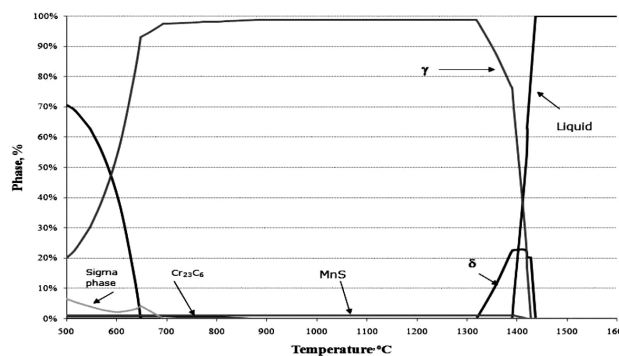


Figure 1: Thermo-Calc calculation of characteristically equilibrium phases for standard AISI 303 depending on temperature

Slika 1: Izračun karakterističnih ravnotežnih faz s programom ThermoCalc za standardno jeklo AISI 303 v odvisnosti od temperature

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3 RESULTS AND DISCUSSION

3.1 Thermo-Calc calculation

Thermo-Calc calculation of the characteristic equilibrium phases for standard AISI 303 depending on the temperature is shown that characteristic non-metallic inclusions in these steels are manganese sulphides types, for which precipitation starts under the liquidus temperature, **Figure 1**.

3.2 Analysis of non-metallic inclusions modified by Te

The shape and composition of inclusions in the standard AISI 303 grade are typical MnS stringers (**Figure 2a**). **Figure 2b** shows the modified spherical shaped inclusions in the modified AISI 303 grade containing 0.033 % Te.⁶

Tellurium occurs in steels in the form of inclusions of manganese (sulpho) telluride ($MnTe_xS_{(1-x)}$), or a white coating of manganese sulphide, or in the form of globular inclusions, which are basically manganese sulphides. The shape of the formation depends on the content of tellurium in steel. It is necessary to take into account the ratio of Mn:S = 4 and Mn:Te = 20. Otherwise, during the hot processing characteristic cracks along the edges of semi-finished products appear.⁷

Figure 3 presents the elemental distribution of typical non-metallic inclusions for the stainless steel AISI 303 modified by Te performed by scanning electron microscope (SEM) Jeol JSM 5610 with attached

Table 2: Chemical composition of modified AISI 303 austenitic stainless steels, in mass fractions (w%)

Tabela 2: Kemijska sestava spremenjenih AISI 303 avstenitnih nerjavnih jekel, v masnih odstotkih (w%)

Type of AISI 303	C	Si	Mn	P	S	Cr	Ni	Te	Zr
by Te	0.05	0.40	0.80	0.010	0.16	18.9	9.3	0.033	–
by Te+Zr	0.03	0.47	0.72	0.012	0.18	18.5	8.9	0.040	0.007

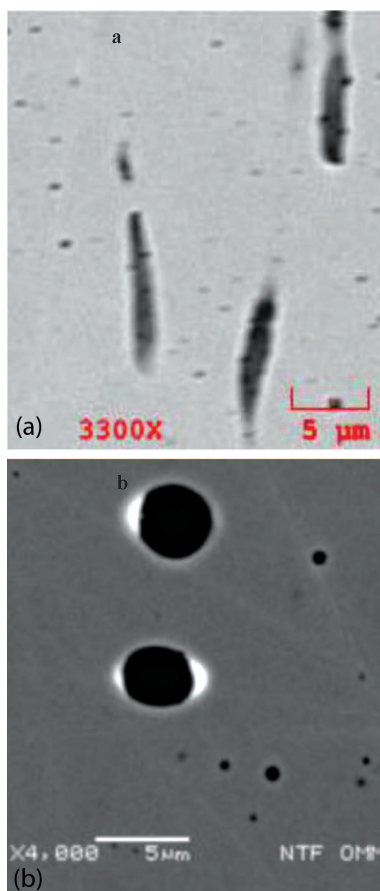


Figure 2: Typical shape of MnS inclusions: a) MnS stringers in standard AISI 303, b) spherical MnS inclusions by Te outlayer (bright colour) in modified AISI 303

Slika 2: Tipične oblike vključkov MnS (PSE): a) razpotegnjeni vključki MnS v standardnem jeklu AISI 303, b) sferični vključki s plastjo Te (svetla barva) v modificiranem jeklu AISI 303

energy-dispersive X-ray spectroscopy (EDS) system Gresham Scientific Instruments Ltd., Model No.: Sirius 10/SUTW at an accelerating voltage of 15 kV. EDS maps show an increase of the concentration of Mn and S, which means that these are manganese sulphides enriched around by Te. By means of additional research of sulphides it has been established that these are pure manganese sulphides with the atomic ratio Mn:S= 1:1.

Figure 4 presents a finding that there is a sharp change in composition at the interface of the MnS inclusion and matrix, with evidence of a Te-enriched zone (white colour) around the MnS inclusion. There are tellurides based on Fe and Cr.

Table 3 shows the results of an energy-dispersive spectroscopy EDS analysis at site of interest 1 in **Fig-**

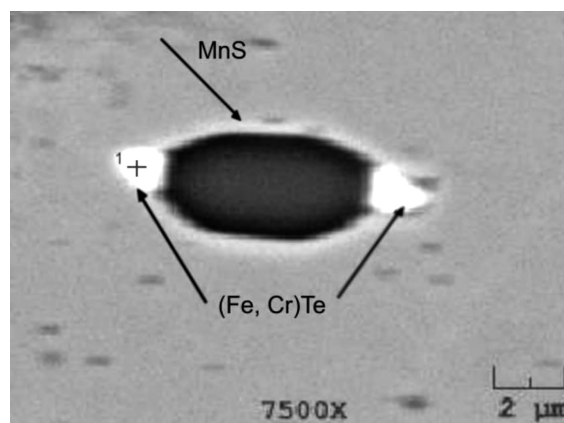


Figure 4: Modified spherical shaped MnS with Te-outer layer (white colour) in AISI 303 modified by Te

Slika 4: Modificiran sferičen vključek MnS obdan s plastjo Te (svetle barve) v jeklu AISI 303, modificiranem s Te

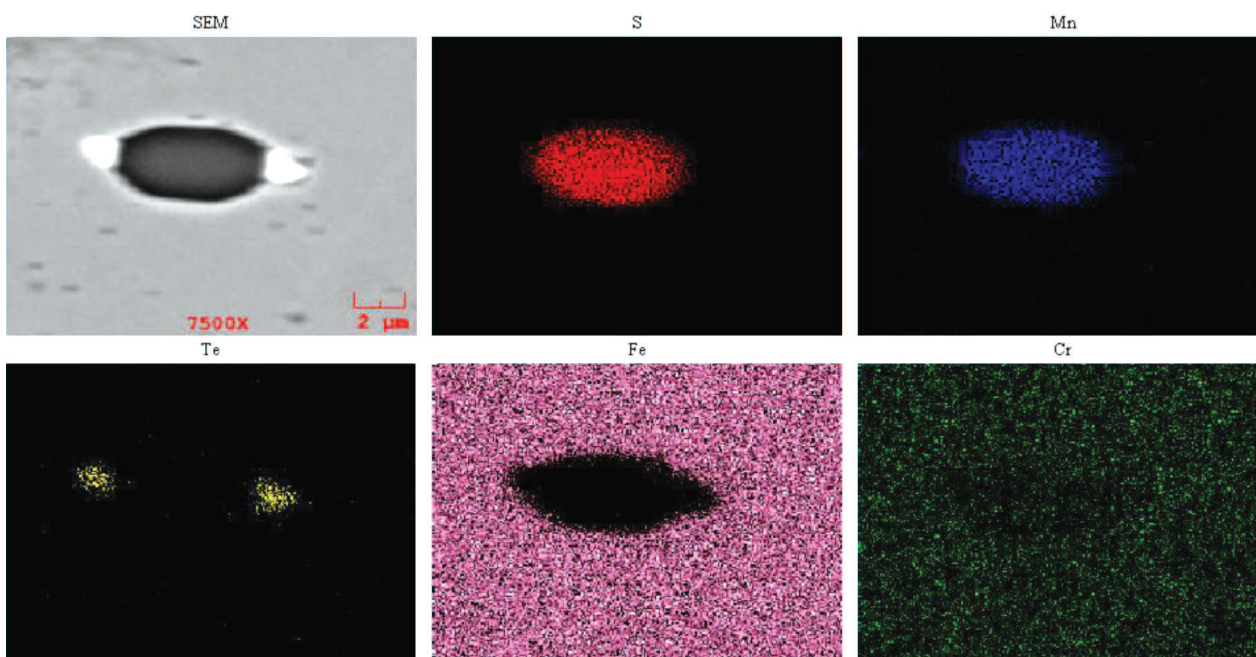


Figure 3: EDS maps of S, Mn, Te, Fe, Cr of non-metallic inclusion in AISI 303 stainless steel modified by Te

Slika 3: EDS-slike porazdelitve elementov S, Mn, Te, Fe Cr s PSE sliko nekovinskega vključka v jeklu AISI 303, modificiranem s Te

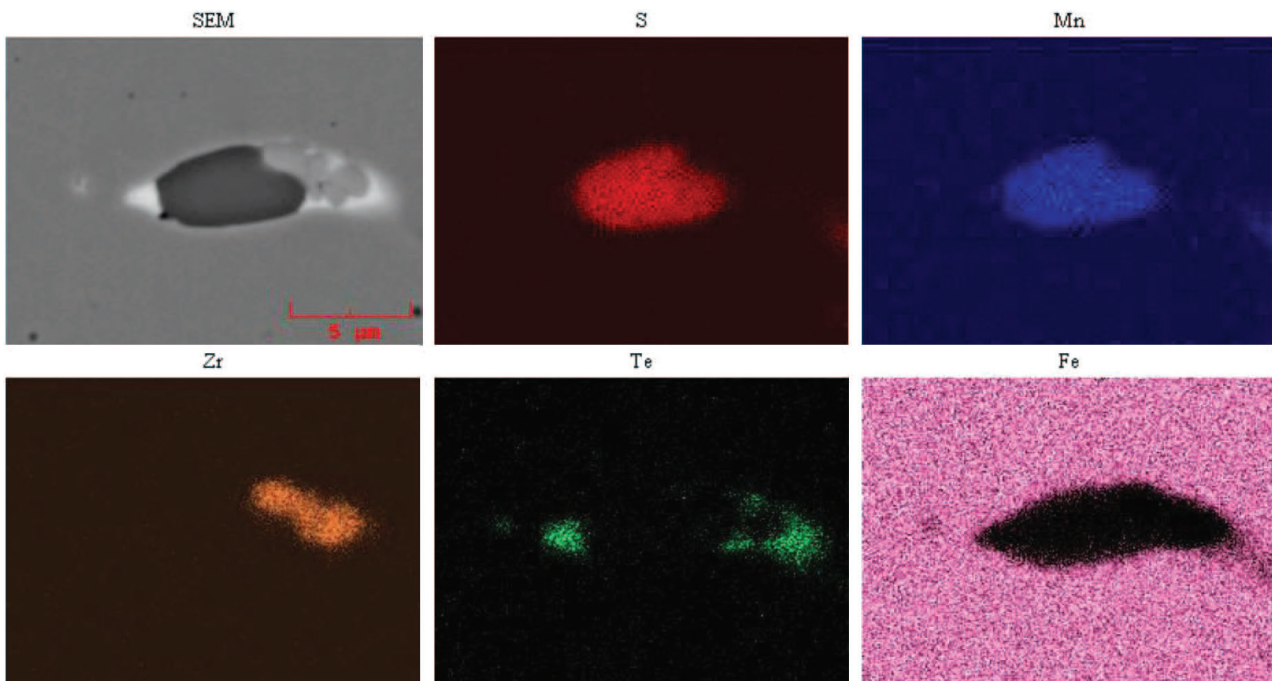


Figure 5: EDS maps of S, Mn, Te, Fe, Zr of non-metallic inclusion in AISI 303 stainless steel modified by Te and Zr

Slika 5: EDS-slike porazdelitve elementov Mn, S, Zr, Te, Fe s PSE sliko nekovinskega vključka v jeklu AISI 303 modificiranjem s Te in Zr

ure 4, as well as the enrichment on Fe and Cr traversing the telluride

Table 3: Results of EDS analysis from the site of interest 1 in **Figure 4**, traversing the telluride

Tabela 3: Rezultati EDS-analize na mestu 1 na **Sliki 4**

Chemical element in site 1	Atomic %
Fe	33.31
Cr	30.44
Te	20.44
Mn	3.81
S	4.63
O	1.42
Cu	1.04
Ni	3.59
Si	0.72
Mo	0.57

3.3 Analysis of non-metallic inclusions modified by Te and Zr

In the case of stainless steel AISI303 modified by Zr and Te an investigation into the behaviour of transition metals like zirconium is carried out. Zirconium is used as a micro-alloying element, because it is strongly affined to sulphur and oxygen.⁶

Elemental distributions of typical non-metallic inclusions in modified AISI 303 by Te and Zr, are presented in **Figure 5**. There is also evidence of an enrichment of the elements S, Mn, Te and Zr.

Around sulphide inclusions MnS (black colour) can be noticed a sharp transition to the higher Te-ratio

around the sulphide particle as well as a Zr-enriched zone connected to a sulphide inclusion.

Zirconium can affect the shape of manganese sulphide inclusions, causing the inclusions to be spherical rather than elongated. In high-chromium steel like AISI 303, zirconium can form complex precipitates that can occur in micro-segregation bands. The SEM micrograph (**Figure 6**) shows the multiple or connected inclusion in stainless steel AISI 303 modified by Te and Zr. These typical mixed inclusions consist usually of three constituents: manganese sulphide as main inclusion part with outer parts of zirconium sulphide/oxide particles and telluride based on Cr.

Table 4 shows an EDS results from the site of interest 1 (**Figure 6**) traversing the zirconium particles. By means of additional research of oxide/sulphides it has been established that those are based on zirconium with the atomic share Zr(S,O).

The modifications of non-metallic inclusions are considered to obtain a desired balance between mechanical properties and machinability. It should be pointed out that the total effect of different inclusions on the machinability and final mechanical properties depends on such characteristics of non-metallic inclusions as chemical composition, hardness, deformability, number, size, morphology and distribution in steel.⁸

The existence of MnS particles elongated during forging and hot-rolling in plastic mould steels is a cause of increasing the anisotropy of mechanical properties. The control of MnS particles with the additions of Ti, Cr, Zr, etc. has been studied to suppress the anisotropy of

mechanical properties and to ensure a uniform workability.^{9–11} H.-H. Kim et al.⁹ have investigated that the Zr addition controls the elongation of MnS particles by forming MnS-Zr₃S₄ compound in a steel containing a large amount of sulphur (0.25–0.35 %S). T. Sawai et al.^{10,11} have reported that the coexistence of Mn-Si oxide particles and ZrO₂ particles can contribute to disperse fine MnS particles by acting as nucleation sites of MnS particles. The controlled MnS shape by the Zr addition improves the anisotropy of mechanical properties according to the distribution of MnS and Zr particles.¹²

Also, the shape and chemical change of MnS particles was observed by adding Te and Zr. Te and Zr addition controls the elongation of MnS particles by forming a complex compound in the stainless steel without significant reduction of mechanical properties. Both modified steel grades have mechanical properties (R_m 635–630 N/mm², KV 62–65 J) that are characteristic for AISI 303 standard grade. The modified machinability improved the steel grade with Te (cutting force 400 N) has up to 15 % better machinability compared to AISI 303 standard grade, and grade with Zr and Te (cutting force 360 N) has up to 25 % better machinability compared to AISI 303 standard grade (cutting force 459 N).

The modified machinability improved the steel grade with Te and Zr shows the structural and chemical changes of MnS according to the formation of complex inclusions.

Table 4: Results of EDS analysis from the site of interest 1 and 2 in **Figure 6**, traversing the zirconium particles (site 1) and telluride (site 2)

Tabela 4: Rezultati EDS-analize na mestu 1 na **Sliki 6**

Chemical element, atomic %	in site 1 (Figure 6)	in site 2 (Figure 6)
Zr	55.19	-
S	11.96	10.68
O	10.57	-
Mn	8.47	11.40
Cr	6.44	31.82
Fe	4.70	15.83
Te	0.94	28.44

4 CONCLUSIONS

In order to produce steels with better machinability, such as AISI 303 grade, the effects of Te and Zr on the modification of inclusions with carefully designed composition are presented.

Thermo-Calc calculation related to AISI 303 shows that the typical inclusions are the precipitates of manganese sulphides.

The manganese sulphide during the plastic deformation get thinner and longer, but by the formation of complex inclusions connected by Te and Zr particles their shape becomes more spherical.

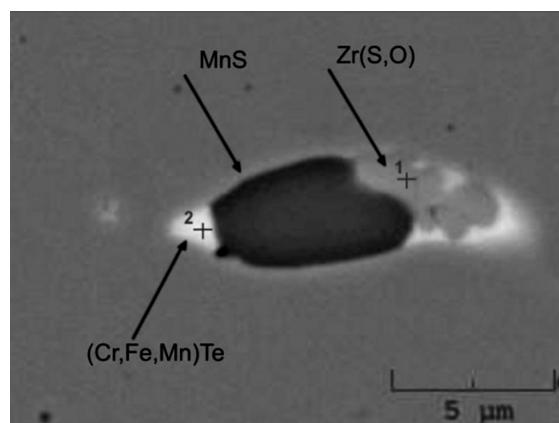


Figure 6: Mixed inclusions: spherical shaped MnS with telluride and zirconium particles in stainless steel AISI 303 modified by Te and Zr
Slika 6: Mešani vključki v nerjavnem jeklu AISI 303, modificiranem s Te in Zr: sferični vključek MnS s telurjevimi in cirkonijevimi delci

By chemical effects on the formation of non-metallic inclusion the nature of inclusions can be changed, thus the strength of the inclusion increases.

The results presented in this paper show that the micro-alloying by Te promoting the retention of spherical-shaped sulphide type inclusions and changing of their chemical composition.

In AISI 303 steel alloyed with Te and Zr the inclusions consist of complex inclusions – manganese sulphide connected on tellurium or that like Zr-oxide-sulphide.

The AISI 303 modified grades have better machinability compared to standard AISI 303 grade and with the mechanical properties in the limits prescribed for the AISI 303 standard grade.

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A. MAHMUTOVIĆ et.: MODIFICATION OF THE INCLUSIONS IN AUSTENITIC STAINLESS STEEL BY ADDING ...

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