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Strengthened Cr-Si-base alloys for high temperature applications

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ABSTRACT

The microstructural development of Cr—Si alloys with Cr ≥ 89 at.% has been studied. As well as silicon, up to 2 at.% germanium, molybdenum, and platinum were used as alloying elements. All alloys consist of only two phases, Cr_{ss} and A15. The phase fraction of primary A15 precipitates present in the arc melted condition and fine secondary A15 precipitates formed after a heat treatment (100 h at 1200 °C) were determined. EPMA and SEM measurements show that the alloying elements partition in different ways: Molybdenum is homogeneously dissolved in both phases, while platinum, germanium, and silicon predominantly act as A15 phase formers. Additionally, molybdenum refines the A15 precipitates, germanium increases the amount of secondary precipitates, and platinum coarsens the microstructure. The lattice parameters of both phases were determined using XRD. The results were found to be in accordance to the elemental partitioning behavior of the constituent phases and can be correlated to the respective covalent atomic radii of the respective alloying element. Microhardness measurements confirmed the alloy's ability of precipitation hardening. Using nanohardness measurements the A15 phase was found to be around 18GPa harder compared to Cr_{ss} offering a way to design mechanical properties depending on alloying element additions, A15 phase fraction, and distribution.

1. Introduction

Nowadays, Ni-base superalloys are the most commonly used high-temperature materials. However, further increases in application temperatures are limited due to the alloy's melting points of around 1350 °C causing softening of single crystalline Ni-base superalloys above 1150 °C [1]. Intermetallic reinforced refractory alloys including the well known Mo-Si-B family and Nb-silicide based alloys are promising candidates for new alloy development due to their higher melting points and their high temperature strength. Among these, the body centered cubic Cr-base alloys offer a lower density, and a higher thermal conductivity compared to Ni-base superalloys, high oxidation resistance, and competitive pricing [2–4]. The main drawbacks are the ductile to brittle transition temperature (DBTT) which is higher than room temperature, oxidation at ultra high temperatures (T ¿ 1000 °C), nitrogen embrittlement at high temperatures, and the weak high temperature strength of chromium [2, 5, 6]. To improve the high temperature strength, alloying additions resulting in a two phase structure with Cr_{ss} phase and a strengthening intermetallic phase such as A15 or Laves phase were investigated by several groups [7–27]. The majority of such studies focuses on eutectic Cr-alloys that allow no or limited deformation such as forging or microstructural optimization after casting.

The present study focuses on Cr—Si alloys with Cr ≥ 89 at.% which offer temperature-controlled precipitate formation and therefore a targeted microstructural design. The influence of Si, Ge, Mo, and Pt additions on the Cr_{ss}-A15 alloy microstructure is investigated systematically aiming at the development of a Cr-base Cr—Si alloy suitable for precipitation hardnening. Ge additions were reported to increase SiO_2 adherence on silicides and thereby improving the oxidation behavior at high temperatures [28, 29]. In eutectic Cr_{ss}-Cr_3Si alloys substituting 2 at.% Si by Ge was found to be highly beneficial to high temperature oxidation and nitridation resistance at 1200 °C and 1350 °C [26, 27]. Additionally, Ge and Si were found to be mutually substitutable in both Cr_{ss} and A15 phases while up to a substitution of 2]at.% the fine nodular eutectic microstructure is maintained. Mo shows promising results concerning the improvement of mechanical properties of Cr and Cr—Si alloys. Raj reported improved creep properties of a two phase $(Cr,Mo)_3Si/(Cr,Mo)_5Si_3$ alloy which was produced by adding around 30 at.% Mo to Cr_3Si [22, 30] while Cruse et al. observed a slight improvement in toughness by alloying Cr_3Si with Mo [23]. Matsumoto et al. showed that alloying pure Cr with 0.2 mol% Mo has a beneficial effect on the room temperature ductility and improved the minimum creep rate up to one order of magnitude [31]. In addition, Mo and Cr show complete miscibility above 880 °C [32] and Mo leads to solid solution strengthening in Cr(Ta)-Cr_2Ta alloys [33–35].

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Pt can be dissolved up to 9.8 at.% in chromium at 1500 °C [36, 37]. Moreover, it has a high solubility dependence on temperature, decreasing to only 1.1 at.% at 500 °C with the Pt in excess also forming an A15 phase (Cr_3Pt) [36, 38]. Hence, alloying a Cr_{ss}-A15 alloy with Pt offers the potential of a high variation in A15 precipitation fraction and therefore the adjustment of mechanical properties depending on heat treatment. All alloys were investigated in the arc melted condition and after a heat treatment at 1200 °C for 100 h. In all cases, the fraction of A15 phase precipitation, the elemental partitioning, and the change of lattice parameter were determined. The impact of microstructural changes on hardness was investigated using nanoindentation and microhardness measurements.

2. Materials and methods

The alloys used in this work were prepared by arc melting using chromium pieces (Cr ¿ 99.95 wt%, Plansee), silicon pieces (Si ¿ 99.999 wt%, GfE), germanium pieces (Ge ¿ 99.999 wt%, Haines & Maassen), molybdenum wire (Mo ¿ 99.97 wt%, Plansee), and platinum pieces (Pt ¿ 99.9 wt%, Hereaus). The melting was conducted in a compact arc melter (MAM-1, Edmund Bühler, Germany) on a water-cooled copper mold under a high purity argon atmosphere. Before melting the Cr-based alloys, a zirconium getter was melted twice to capture the residual oxygen in the chamber. The cast ingots had total weights of around 7 g (droplets with diameter around 10 mm and around 17 mm length) and were remelted five times to ensure homogeneity. The ingots were cut into two pieces parallel to the solidification direction using wire erosion. One specimen was investigated in the arc melted condition and one was studied in the annealed state. Prior to annealing the specimen's cross section was wet ground up to 320 grit (ANSI) and encapsulated in an evacuated quartz glass tube. The encapsulated samples were annealed for 100 h at 1200 °C in a muffle furnace. After heat treatment the samples were quenched in water by simultaneously destroying the quartz glass tubes to ensure quenching of the samples.

The following microstructural and mechanical investigations were carried out in the center of the specimens parallel to the solidification direction in order to enable comparability. All samples, the arc melted and annealed specimens, were mounted in epoxy resin with their cross section face up. The samples were ground with successively finer silicon carbide papers from 120 to 1000 grit (ANSI) and were polished with 3 µm and 1 µm diamond suspensions. Phase analysis was conducted using XRD (X-ray diffraction, Brucker D8 advance diffractometer, with Cu-K_α) of the sample's cross sections. The measurements were conducted by varying 2θ from 20° to 90° with a step size of 0.02° and a 4 s counting time. For XRD pattern analysis the PDF database was used.

The microstructure and the composition of alloys and phases were investigated using optical microscopy, an electron microscope (SEM, Philips XL40 electron microscope) equipped with an energy dispersive x-ray spectrometer (EDX), and an electron probe microanalyser (EPMA, JEOL JXA-8100). The EPMA was used in two imaging modes, backscattered electron microscopy (BSE), and EPMA element distribution maps. The composition of the ingots was analyzed in the arc melted and annealed conditions using quantitative EPMA spot measurements in a 11 × 11 grid with a step size of 1 µm in the x and y directions. The homogeneity of the alloy composition was investigated using four EDX area measurements per sample ($50\,\mu m \times 50\,\mu m$) with 20 kV acceleration voltage and an analyzer distance of 10 mm (Philips XL 40 electron microscope).

EPMA Si element maps were used to determine the area fraction of the A15 phase. The Si element distribution maps were used due to the significant concentration differences of silicon in the A15 phase compared to the Cr_{ss} phase, leading to a significant contrast in the silicon maps. At least five silicon element maps with magnifications of 1000× or 2000× were measured at different positions using a voltage of 15 kV. The pictures were subsequently analyzed using ImageJ 1.51 software [39].

Additionally, hardness measurements were conducted on the annealed alloys using microhardness measurements for overall hardness determination and nanoindentation testing at room temperature. The microhardness measurements (M-400-H, Leco) were carried out in the center of the specimen with a Vickers diamond pyramid indenter, a load of 300 g and a dwelltime of 15 s. To investigate the difference in hardness between the arc melted and annealed condition the measurements were conducted on both conditions. Nanoindentation testing was used for determining the hardness of the individual phases. For a comparison of the alloy's values, nanoindentation was also conducted on pure Cr samples of different purities (Cr ¿ 99.95 wt%, Plansee, and Cr ¿ 99.995 wt%, Alfa Aesar) which were also produced using arc melting as described above. The nanoindentation tester NHT^2, CSM Instruments, Switzerland, equipped with a Berkovich tip was used. The measurements were carried out under a constant load of 20 mN, applying a loading rate of 40 $\frac{mN}{min}$ and an unloading rate of 80 $\frac{mN}{min}$. The nanohardness values (*HIT*) were determined by averaging the data of at least 6 measurements. The hardness is calculated as shown in Eq. (1) using a Berkovich indenter face angle of $\theta = 65.27^\circ$ [40] and h_c as the maximum contact depth.

$$HIT = \frac{P}{3\sqrt{3}\cdot tan^2(\theta)\cdot h_c^2} \approx \frac{P}{24.5 h_c^2} \quad (1)$$

3. Results

3.1. Microstructural investigations

The precipitation behavior of the Cr-rich side of the Cr—Si system was studied on the alloys $Cr_{93}Si_7$, $Cr_{92}Si_8$, $Cr_{91}Si_9$, and $Cr_{90}Si_{10}$ (in at. %). Additionally, the microstructural changes resulting from the addition of ternary elements were investigated using the ternary alloys $Cr_{91}Si_7Ge_2$, $Cr_{90}Si_8Mo_2$, and $Cr_{91}Si_7Pt_2$. The nominal and measured compositions of the studied alloys are listed in Table 1. The amount of Si differs slightly from the nominal concentration due to evaporation of Cr during casting. Especially, for $Cr_{90}Si_8Mo_2$ the Si content is slightly higher compared to the other ternary alloys. The corresponding microstructures in the arc melted and annealed conditions are shown in Fig. 1 and Fig. 2. The observed phases are single phase solid solution Cr_{ss} and Cr_3Si A15 in all cases which is verified by the XRD patterns in Fig. 3 ($Cr_{91}Si_9$ is shown as an example for all binary alloys). In addition, some shrinkage cavities (black) are visible in the cross sections caused by the casting procedure.

In the binary Cr—Si alloys the increase of Si concentration from $Cr_{93}Si_7$ to $Cr_{90}Si_{10}$ alloy leads to a significant change in the microstructure. In the arc melted condition $Cr_{93}Si_7$ and $Cr_{92}Si_8$ showed single phase solid solution microstructures (see Fig. 1(a) and (c)). For silicon concentrations above 9 at.%, Cr_{ss} dendrites formed with branched interdendritic A15 phase rich areas (Fig. 1(e) and (g)) which are referred to as primary precipitates in the following. These areas might be anomalous or divorced eutectics like those observed in hypoeutectic Ni—Sn [41] or Co—Sn alloys [42]. In comparable systems like Fe-Mo-Ti the formation of very fine (nano-scale) solid solution phases in the

Table 1
Measured composition of the studied binary and ternary alloys.

Alloy	Cr/at.%	Si/at.%	Ge/at.%	Mo/at.%	Pt/at.%
$Cr_{93}Si_7$	93.2 ± 0.3	6.6 ± 0.3	–	–	–
$Cr_{92}Si_8$	92.0 ± 0.2	7.9 ± 0.2	–	–	–
$Cr_{91}Si_9$	90.9 ± 0.3	9.1 ± 0.3	–	–	–
$Cr_{90}Si_{10}$	90.0 ± 0.4	9.6 ± 0.4	–	–	–
$Cr_{91}Si_7Ge_2$	90.7 ± 0.2	7.0 ± 0.1	2.2 ± 0.2	–	–
$Cr_{90}Si_8Mo_2$	89.9 ± 0.6	7.8 ± 0.5	–	2.0 ± 0.1	–
$Cr_{91}Si_7Pt_2$	90.9 ± 0.3	6.7 ± 0.2	–	–	2.1 ± 0.1